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Element Transport in A River-lake Continuum across Forest-dominated Landscapes: A Case Study in Central Louisiana

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ELEMENT TRANSPORT IN A RIVER-LAKE CONTINUUM ACROSS FOREST-DOMINATED LANDSCAPES: A CASE STUDY IN CENTRAL LOUISIANA

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ABSTRACT

Studying the biogeochemical connectivity between rivers and lakes can help us understand their ecological and environmental impacts within a drainage basin, which is especially true for forest watersheds that play a vital role in provisioning freshwater services to ecosystems and downstream communities. This dissertation research consists of three interconnected studies with the overarching goal of discerning the connectivity of elements in a river-lake continuum across forest-dominated landscapes. These studies utilized water samples and in situ measurements collected from the Little River-Catahoula Lake continuum in the subtropical Louisiana, USA at monthly intervals during 2015-2016 and 1978-2008 historical water quality, hydrological and meteorological data downloaded from public-access databases to determine whether the forestry best management practices (BMPs) were effective in reducing levels and loads of sediment and nutrients from forest-dominated river headwaters and investigate the transport of dissolved carbon and metals from a river upstream to the outlet of its downstream receiving lake. Results show that forestry BMPs were effective in reducing sediment runoff from the intensively managed forested headwaters but less effective in controlling stream nitrogen concentrations and loading. Phosphorus loading at the basin outlet was significantly increased, which was probably caused by a drastic increase in the application of phosphorus fertilizer after extensive BMPs implementations. The dissolved organic carbon (DOC) pool in the studied watershed was dominantly terrestrially derived, while autochthonous DOC production derived from aquatic phytoplankton during the warm productive period was also important. In contrast, dissolved inorganic carbon (DIC) in the studied river-lake continuum was mainly from carbon-13 isotope (^{13}C) depleted sources such as soil respired CO_2 and in situ organic matter, and the combined effect of metabolism and carbon dioxide outgassing controlled

the DIC dynamics in the in-network lake. For all metals analyzed in this study, the river functioned as a sink for Al, Ca, Fe, K, Mg, Na, B, Ba, Mn, Sr and Ti due to sedimentation and biological immobilization, while the lake acted as a source for Al, Mg, K and Ti due to their enrichments in the lakebed, a greater weathering intensity at the lake and backwater effects.

CHAPTER 1. INTRODUCTION

1.1. BACKGROUND

Rivers and lakes are the veins linking terrestrial and aquatic ecosystem across landscapes. Rivers carrying suspended and dissolved materials from the land to the ocean are the principal link in transferring elements between these systems (Wafar et al., 1989; Gong et al., 2015). The transfer of riverine materials at the Earth's surface plays a key role in the carbon balance at the decadal to centennial scale, the sediment transport, the nutrient balance of surface waters, and controls the coastal zone functioning to a great extent (Milliman et al., 1987; Martin and Windom, 1991; Caddy and Bakkun, 1994; Meybeck, 2003).

Lakes have been recognized as 'hot spots' within riverine systems for the trapping and cycling of elements. In a river-lake network, lakes have been found to remove nitrogen (Harrison et al., 2009) and carbon substantially (Cole et al., 2007; Bastviken et al., 2011). Recent landscape modeling studies at basin- and global-levels have indicated substantial retention of elements by reservoirs in aggregate, suggesting these ecosystems could be more influential to downstream element delivery than previously thought (Harrison et al., 2009; Brown et al., 2011; Powers et al., 2014; Powers et al., 2015). Nowadays lakes are increasingly being studied in the context of biogeochemical connectivity across waterscapes (Winter, 1999; Jones, 2010; Lottig et al., 2011; Lottig et al., 2013), which remains an emerging research frontier (Powers et al., 2014).

Substantial progress has been made recently for a holistic view of element cycles in river and lake systems. For instance, as opposed to the view in the literature from the 1970s and 1980s that generally assumed inland waters as a passive pipe simply transporting terrestrial materials conservatively to the ocean (e.g., Garrels and Mackenzie, 1971; Meybeck, 1982), studies in the past decade have conceptualized inland waters as an active pipe receiving, processing and storing

terrestrial materials during its travel (e.g., Cole et al., 2007; IPCC, 2013; Tranvik et al., 2018). However, a knowledge gap still exists in hydrological connectivity and the exchange of matter, energy and biota via river corridors across waterscapes (Ward et al., 2002; Tranvik et al., 2018), and rigorous investigations of that are still needed to provide insights into effects of waterscape-level functional processes on element dynamics in diverse river-lake systems.

Carbon, required by all aquatic organisms, is one of the most concerned elements in aquatic geochemistry studies. Dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) together constitute the major carbon reservoir in rivers and lakes, which have been recognized as important components of the global carbon cycle interacting with atmospheric, terrestrial and oceanic carbon (Brunet et al., 2005; Shin et al., 2015). DIC is often the most abundant inorganic carbon phase in rivers and streams in aquatic ecosystems (Marx et al., 2017), while DOC plays an important role in affecting the transport of metals and organic pollutants, influencing photo-chemistry of natural waters and nutrient availability and serving as an important source of microbial substrate (Hope et al., 1997; Battin et al., 2009). Previous studies have recognized the importance of identifying the source and fate of DIC and DOC in surface water transport to elucidate carbon cycling through atmosphere–land–ocean systems (Volk et al., 1997; Maurice and Leff, 2002; Mayorga et al., 2005; Miller, 2011). The species and magnitude of dissolved carbon exchanges within these systems can be determined through the concentration and carbon isotopic composition of DIC ($\delta^{13}C_{DIC}$) and DOC ($\delta^{13}C_{DOC}$) in waters (Telmer and Veizer, 1999; Ye et al., 2015).

The transport of major and trace metals in inland waters could also have a great environmental and ecological impact to aquatic systems. The weathering of minerals has been traditionally considered as the most important factor in element transports in rivers and lakes

(Martin and Meybeck, 1979; Roy et al., 1999), while biologic and anthropogenic activities have also been claimed to play an increasing role to the water chemistry in the recent decades (Drever, 1994; Lopez1 et al., 2006; Kang et al., 2019). Certain metals (e.g., Ca, Mg, Fe) have been reported to be fundamental in supporting structural development of organisms and primary production (Ludwig, et al., 2009; Meybeck, 1982; McLaughlin and Wimmer, 1999; Rabalais, 2002), while some heavy metals have been recognized to produce considerable harm to environment and human health (Naimo, 1995; Jezierska et al., 2009). The characterization of spatial and temporal variability of metal cycling in rivers and lakes is crucial to identify sources and sinks of metals as well as their transport modes and to understand the coordination of biological, geological and chemical factors in these processes.

However, our knowledge is limited about the dissolved carbon transport and metal chemistry of water across a river-lake continuum. Lakes and rivers have been traditionally studied as separate entities for dissolved carbon transport, with rivers being considered as either a single channel of flowing water or as a larger system including the river channel floodplain network (Bouwman et al., 2013). For example, riverine carbon transport is mostly studied as a continuous system from headwaters to the river mouth without considering in-network lakes within rivers' passageways (Dubois et al., 2010; Iwata et al., 2013). Existing studies focusing on riverine DIC have reported that partial pressure of carbon dioxide (pCO_2) in rivers and streams can decrease downstream because of CO_2 evasion as water travels away from high CO_2 inputs (Brunet et al., 2009), or increase downstream if originates in large lakes (Buhl et al., 1991; Flintrop et al., 1996). However, very few studies have looked into how DIC dynamics change in a fluvial system before and after passing through a lake. For DOC, while extended residence times in lakes could result in lakes functioning as DOC sinks, results to date have been

inconsistent indicating that lakes can function as both sources (Kalinin et al., 2016) or sinks (Kang et al., 2016) of DOC. In addition, most studies for dissolved carbon dynamics have been undertaken in Nordic or temperate regions (Pacheco et al., 2014; Chow et al., 2017), but their results may not necessarily reflect the same as a subtropical watershed study. Similar conditions also apply to metals. Existing studies of metal dynamics considering the biogeochemical connectivity between lakes and rivers were mostly looking at sediment metals (Ilina et al., 2016; Thorslund et al., 2017), the results of which may not be applicable for a metal chemistry study of water. Only a few studies were conducted recently reporting the metal distribution in water in the river-lake system (e.g., Ciazela et al., 2018). To my knowledge, up to now no study has been conducted for metal transports in water from the upstream of an inflow river to the outflow of a lake within the connected fluvial network.

In addition, forested watersheds play a vital role in provisioning fresh water services to ecosystems and downstream communities (Lowe and Likens, 2005; Caldwell et al., 2016; Duan et al., 2018). It has been reported that forest watersheds provide 80% of freshwater resources in the USA (Ice and Binkley, 2003; US EPA, 2000), and about a third of the world's largest cities receiving a significant proportion of drinking water from forests (Dudley and Stolton, 2003). Waters from forested landscapes are generally considered of high quality, but that may not be the case with industrial forest land (Anderson and Lockaby, 2011; Ice et al., 1997). Forest operations, such as harvesting, yarding, road construction, and site preparation, can have adverse impacts on water quality of adjacent water bodies (Appelboom et al., 2002; Morris et al., 2015; Wear et al., 2013). Surface soil erosion has been cited as the most important water quality concern related to forest practices in the USA (Binkley and Brown, 1993; Yoho, 1980), which not only has profound effects on stream headwater environments but may also have substantial

effects on areas far downstream due to the capability of suspended sediments to travel exceptionally long distances (Hotta et al., 2007). Nutrient pollution caused by silvicultural activities in forest waters is also an issue. Early experimental studies of nutrient responses to timber harvest have reported dramatic nutrient increases in forest waters after harvesting (Likens et al., 1970). In consequence, water quality in forested watersheds has received more and more attention in the recent decades.

Forestry best management practices (BMPs) are implemented as a result to prevent or reduce the adverse impacts of forest activities on water quality while permitting the intended forest management activities to occur (Wang et al., 2004). Although significant research efforts have been conducted aiming at verifying the effectiveness of forestry BMPs, most of them were taken at the plot scale and/or for short terms (Anderson and Lockaby, 2011; Aust and Blinn, 2004; Cristan et al., 2016). This is especially the case for the Southern Coastal Plain region of the USA, home to some of the most productive forests in the USA which are intensively managed for forest production. It has been reported that forest operations accounted for 5900 km of impaired rivers and streams in the Southern USA, with the majority of more serious water quality problems located in Louisiana, Mississippi, and Oklahoma (West, 2002; NASF and SAF, 2000). In this context, the South would likely be the optimal region to evaluate the extent and nature of the water quality impacts of forest operations. However, very few studies have examined the long-term effectiveness of forestry BMPs in the Gulf Coastal Plain region, and none exists for the state of Louisiana at a basin scale.

1.2. RESEARCH OBJECTIVES AND HYPOTHESES

Motivated by that, this dissertation research investigated element transports in a river-lake continuum across a forest-dominated landscape (Figure 1.1). The research was conducted in the Little River Basin in Central Louisiana, whose environmental conditions are widely representative for the Subtropical Division in Ecoregions of the United States. Specific objectives of the research are to:

1) Determine whether the current forestry BMPs of Louisiana are effective in reducing sediment, nitrogen, and phosphorus levels and loads from forest-dominated river headwaters.
2) Investigate the major sources and corresponding biogeochemical processes controlling DIC and DOC dynamics in a river-lake continuum and explore whether the in-network lake function as a carbon sink or carbon source for dissolved carbon transport across the waterscape.
3) Assess the spatial and seasonal dynamics of major and trace metal concentrations and their atomic ratios from a river upstream to the outlet of its downstream receiving lake and elucidate whether the lake and river act as a source or a sink for metal dynamics.

Three main hypotheses were made:

1) Long term forestry BMPs of Louisiana are effective in reducing sediment runoff and phosphorus transport but less effective in controlling stream nitrogen concentrations and loading.
2) The DOC pool in the Little River Basin is mainly terrestrially derived, while DIC dynamics are heavily affected by metabolism and CO_2 outgassing, making the in-network lake a sink for dissolved carbon transport.

3) The Little River functions as a sink for metal transport mainly due to sedimentation and biological immobilization, while Catahoula Lake acts as a metal source due to a greater weathering intensity in the lake.

1.3. STUDY AREA AND RESEARCH APPROACH

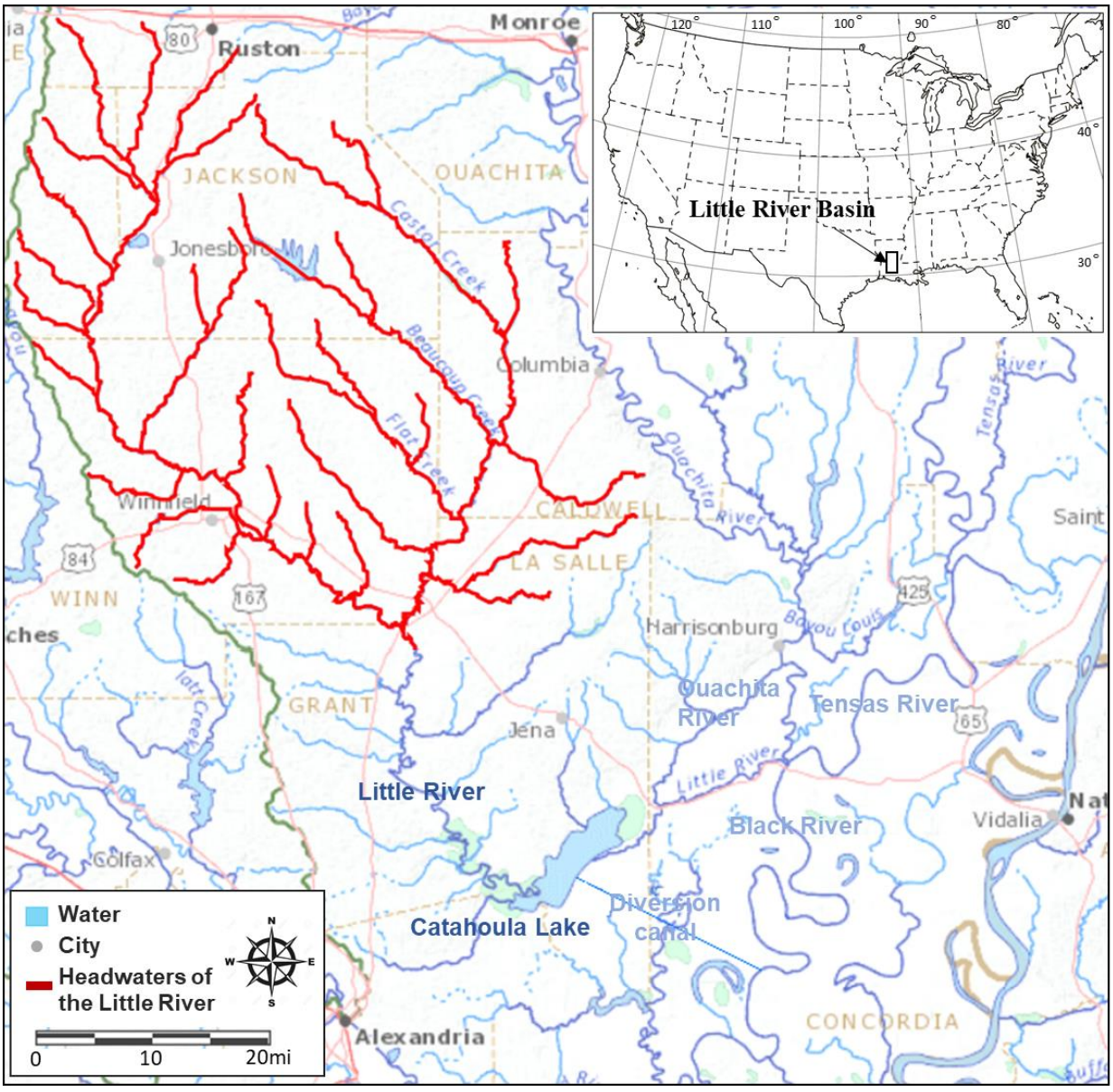

Figure 1.1. Geographical location of the Little River Basin in subtropical Louisiana, the United States.

The Little River is formed by the confluence of the Dugdemona River and Castor Creek, which together drain drains an area of approximately 5000 km^2 land in central Louisiana, at a geographical location of 92° 21′ 46″ W and 31° 47′ 48″ N (Figure 1.1). The river flows initially southeastwards in north-central Louisiana, and then turns east-northeastwards into Catahoula Lake, the largest natural inland freshwater lake in Louisiana with a surface area of approximately 119 km^2 (Figure 1.1). A check dam was built across the natural outflow at the French Fork of the Little River to prevent outflow from the lake or backwater from the Black River, and the lake mainly drains through a straight channel of approximately 30 m to the Black River (Figure 1.1). Headwaters of the Little River are predominantly forested and mainly affected by intensively managed industrial forest activities (Mast and Turk, 1999; DaSilva et al., 2013). The uppermost part of the Little River above Catahoula Lake flows through a mixed oak-gum bottomland forest interspersed with stands of bald cypress (Gaydos et al., 1973; LDEQ, 2002). Voluntary forestry BMPs were developed by the State of Louisiana in 1988 (Bourland 1988) and revised in 2000 (LDAF and LDEQ 2000) to protect water quality during forestry operations.

To investigate the aforementioned questions, monthly field trips were made to conduct in situ measurements as well as to collect water samples from February 2015 to February 2016 at four sites representing the Little River-Catahoula Lake continuum. They include a Little River upstream site close to the confluence point of the Dugdemona River and Castor Creek where the Little River exits the forested headwater region, a lake inflow site located approximately 2,500 m upstream of the western lakeshore wetland, a lake outflow site on the outflow canal about 500 m downstream of the south-central lakeshore, and a French Fork of the Little River site which was about 900 m west of the check dam (Figure 1.2). Climate, water quality and hydrological data from 1978 to 2016 were also collected from various stations administrated by United States

Geological Survey (USGS), United States Army Corps of Engineers (USACE), Louisiana Department of Environmental Quality (LDEQ), National Oceanic and Atmospheric Administration (NOAA) and Southern Regional Climate Center (SRCC).

Figure 1.2. Photos of the four sampling sites in Little River-Catahoula Lake continuum. Photo courtesy of Zhen Xu and Kaci Fisher.

1.4. SYNOPSIS OF CHAPTERS

Research findings and discussions towards the objectives are broken down into three chapters:

1) Chapter two compared long-term concentrations and loadings of total suspended solids (TSS), nitrate/nitrite nitrogen (NO_3NO_2–N), total Kjeldahl nitrogen (TKN), and total phosphorus (TP) before (1978–1988) and after extensive implementation of forestry BMPs

(1994–2008) at the outlet of headwaters of the Little River Basin that is predominately covered by intensively managed pine forests. This chapter has been published on *Environmental Monitoring and Assessment*. Permission to reprint chapter two has been attached in Appendix A. The publisher is acknowledged as the original source at the bottom of the first page of chapter two.

2) Chapter three explored the connectivity of dissolved carbon in a subtropical Little River-Catahoula Lake continuum from April 2015 to February 2016 and discerned the role of the in-network lake. This chapter has been published on *Science of The Total Environment*. I as one of the authors retain the right to include it in my dissertation (Appendix B). Although a permission is not required, the journal is referenced as the original source at the bottom of the first page of chapter three, as requested by the publisher.
3) Chapter four presented dynamics of total recoverable metal concentrations and their molar ratios along the low-gradient Little River-Catahoula Lake continuum from February 2015 to January 2016 to understand metal biogeochemistry across the waterscape. This chapter has been submitted for peer review.

Chapter two, three and four are written as stand-alone manuscripts for peer-reviewed journals, for which reason there will be some repetitions among these chapters.

CHAPTER 2. ASSESSING EFFECTIVENESS OF LONG-TERM FORESTRY BEST MANAGEMENT PRACTICES ON STREAM WATER QUALITY AT A BASIN SCALE - A CASE STUDY IN SOUTHERN USA

2.1. INTRODUCTION

The degradation of water quality in various water bodies is one of the world's most concerning environmental problems. Several decades of research have demonstrated that water quality degradation is strongly associated with land-use activities, such as intensive agriculture and forest practices (Hewlett et al., 1984; Likens et al., 1970), urbanization (Foley et al., 2005), and building and road construction (Kreutzweiser et al., 2005). Agricultural and forestry activities can increase erosion and sediment loads, and leach nutrients and chemicals to groundwater, streams, and rivers (Carpenter et al., 1998; Foley et al., 2005; McCoy et al., 2015). Urbanization substantially degrades water quality, especially where wastewater treatment is absent (Foley et al., 2005). The resulting degraded water quality has led to dissolved oxygen depletion (Giri and Qiu, 2016; Ice and Sugden, 2003), increased algal blooms (Tsegaye et al., 2006), impairments to water supplies (Foley et al., 2005) and a growth of waterborne disease (Bennett et al., 2001; Townsend et al., 2003).

Waters from forested landscapes are generally considered of high quality, but that may not be the case with industrial forest land (Anderson and Lockaby, 2011; Ice et al., 1997). Forest operations, such as harvesting, yarding, road construction, and site preparation, can have adverse impacts on water quality of adjacent water bodies (Appelboom et al., 2002; Morris et al., 2015; Wear et al., 2013). Surface soil erosion has been cited as the most important water quality

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concern related to forest practices in the United States (Binkley and Brown, 1993; Yoho, 1980), which has profound effects not only on stream headwater environments, but may also have substantial effects on areas far downstream due to the capability of suspended sediments to travel exceptionally long distances (Hotta, 2007). Nutrient pollution caused by silvicultural activities in forest waters is also an issue. Early experimental studies of nutrient responses to timber harvest have reported dramatic nutrient increases in forest waters after harvesting (Likens et al., 1970). Since forest watersheds provide 80 percent of freshwater resources in the United States (Ice and Binkley, 2003; US EPA, 2000), water quality in forested watersheds has received more and more attention in the recent decades. As a result, forestry best management practices (BMPs) are implemented to prevent or reduce the adverse impacts of forest activities on water quality while permitting the intended forest management activities to occur (Wang et al., 2004).

There have been significant research efforts aimed at verifying the effectiveness of forestry BMPs, although most of them were conducted at the plot scale and/or for short terms (Anderson and Lockaby, 2011; Aust and Blinn, 2004; Cristan et al., 2016). Forestry BMPs are usually region-specific, but most of them share similar prescriptions. Most previous studies (e.g. Cristan et al., 2016) have demonstrated that when constructed correctly and in adequate numbers, forestry BMPs reduced negative impacts on water quality, including surface erosion (Auther et al., 1998; Brown et al., 2013; Lang et al., 2015), nutrient runoff (Dahlgren, 1998; Hewlett et al., 1984; McBroom et al., 2008; Secoges et al., 2013; Stednick, 2008; Wynn et al., 2000), and help protect stream biologic integrity (DaSilva et al., 2013; Vowell, 2001). Implementation rates and quality are critical to BMP effectiveness, which can be enhanced with pre-operation planning and with the involvement of registered professionals (Cristan et al., 2016). However, in contrast

to the large number of detailed studies on the short-term effectiveness of BMPs at the plot scale, only limited attention has been given to the long-term performance of BMPs at a basin scale.

This is especially the case for the southern Coastal Plain region of the U.S., home to some of the most productive forests in the U.S. which are intensively managed for forest production. Southern forests are a vital factor in maintaining and improving water quality in the South, and their watersheds have consistently been shown to have lower sediment and nutrient yields with better aquatic biological conditions than non-forested watersheds (West, 2002). However, the wide application of forestry management operations in combination with the abundant water resources in the region increases the potential for water quality impacts (Grace, 2005). It has been reported that forest operations accounted for 5,900 km of impaired rivers and streams in the South, with the majority of more serious water-quality problems located in Louisiana, Mississippi and Oklahoma (West, 2002; NASF and SAF, 2000). In this context, the South would likely be the optimal region to evaluate the extent and nature of the water quality impacts of forest operations. As discussed above, numerous short-term and/or plot-scale studies have been undertaken to evaluate the effectiveness of forestry BMPs, but their results may not necessarily reflect the same as a watershed or river basin scale study. In addition, some effects found from those plot-scale and/or short-term studies are not necessarily observable on long-term basin scale cases. To our knowledge, very few studies have examined the long-term effectiveness of forestry BMPs in the Gulf Coastal Plain region, and none exists for the state of Louisiana at a basin scale.

Therefore, to gain a better understanding about the effectiveness of forestry BMPs in the South and Southeast United States, this study was conducted in a forestry dominated basin in central Louisiana to assess the long-term effectiveness of forestry BMPs. According to the

manual of recommended forestry BMPs for Louisiana, forestry BMP compliance in the state was below 10% before 1989, and increased steadily to more than 80% by 1994 (LDAF and LDEQ, 2000). Based on the information, this study compared the long-term response of stream water quality to industrial forest operations before (1978-1988) and after (1994-2008) the extensive implementation of forestry BMPs. The goal of this study was to determine whether the current forestry BMPs are effective in reducing sediment, nitrogen, and phosphorus levels and loads at a basin scale. The corresponding hypothesis was that long-term forestry BMPs of Louisiana were effective in reducing sediment runoff and phosphorus transport but less effective in controlling stream nitrogen concentrations and loading.

2.2. METHODS

2.2.1. Site Description

In this study we gathered 1978-2008 historical records on water quality of the Little River that drains an area of approximately 5,000 km^2 land in central Louisiana, United States. The Little River is formed by the confluence of the Dugdemona River and Castor Creek, which together drain approximately two-third of the Little River basin, at a geographical location of 92°21'46" W and 31°47'48" N. The river flows initially southeastwardly in north-central Louisiana and turns east-northeastwardly into Catahoula Lake (Figure 2.1). The basin is composed of rounded hills in the north, flat-lying deposits in the central region, and dissected terrace deposits in the south. Specifically, the uppermost part of the Little River above Catahoula Lake flows through a mixed oak-gum bottomland forest interspersed with stands of bald cypress (Gaydos et al., 1973; LDEQ, 2002). Climate in the Little River Basin can be classified as humid subtropical with long hot summers and short mild winters. The long-term annual precipitation is

about 1,470 mm, of which about one quarter travels as surface runoff to streams (Gaydos et al., 1973).

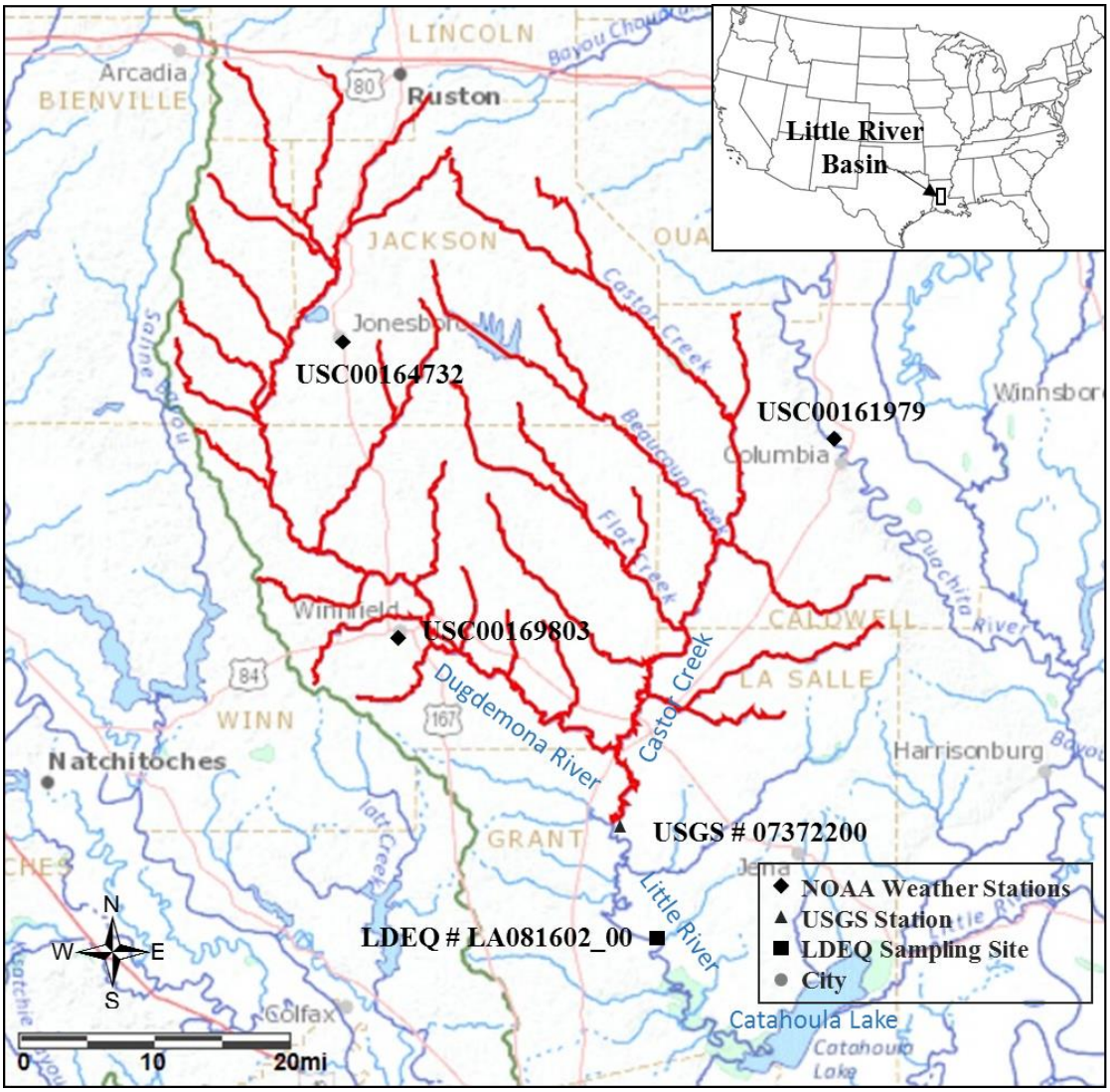

Figure 2.1. Geographical location of the Little River Basin and its headwaters (in red lines) in Louisiana, the United States.

2.2.2. BMP Implementation and Separation of Two Analysis Periods

Headwaters of the Little River are mostly forested and mainly affected by intensively-managed industrial forest activities (DaSilva et al., 2013; Mast and Turk, 1999). Voluntary forestry BMPs were developed by the State of Louisiana in 1988 (Bourland, 1988) and revised in 2000 (LDAF and LDEQ, 2000) to protect water quality during forestry operations. Since the

implementation of forestry BMPs, the Louisiana Department of Agriculture and Forestry has completed eight surveys, with BMP compliance rates reported as <10%, 51%, 80%, 83%, 96%, 96%, 96%, 74% (95%) in 1988, 1991, 1994, 1997, 2000, 2002, 2003 and 2009, respectively. It is worth noting that although the 2009 BMP survey (Kaller, 2009) reported a decline in full BMP implementation rates (74%), over 95% of individually rated BMPs met or exceeded minimum BMP requirements, which is comparable with previous surveys. Therefore, in this study, we divided the 1978-2008 timespan into two periods: a pre-regulation period from 1978 to 1988 and a post-regulation period from 1994 to 2008. We did not include data from 1989 to 1993 in this study in order to avoid possible interference from the transitional time from no BMP implication to full BMP implementation. Additionally, the variability in land use changes was relatively small during the study period (Mast and Turk, 1999), and annual production of sawtimber was reported to remain relatively constant in the regulation years (Nature Conservancy, 2007). Based on those governmental reports and the confirmation from the landowner of the forestland (Plum Creek Timber, Inc.), it was assumed that changes in variability of harvest intensity were not significant during the studied period.

Louisiana's forestry best management practices include a series of guidelines for forest operations during the entire rotation, from timber harvesting to site preparation, reforestation, fertilization, and other silvicultural treatments. Streamside management zones (SMZ) were identified and delineated during pre-harvesting planning, and flagged and marked adjacent to all perennial and intermittent streams before harvesting. In the studied region, SMZs are generally 10.7 m for intermittent streams, and 15.2 m and 30.5 m for perennial streams that are less and more than 6.1 m in width, respectively. Harvesting can occur within the SMZs of perennial streams, and precautions were given along perennial streams to protect the remaining trees

within the SMZs. Roads were located outside the SMZs. During harvesting, trees were felled directionally away from water bodies. Log landings were located where skidding would avoid road ditches and sensitive sites to have a minimal impact on the natural drainage pattern. For regeneration, intensive site preparation activities were avoided on steep slopes or highly erosive soils, and not allowed to enter SMZs and cross stream channels (Brown 2010; LDAF and LDEQ 2000).

2.2.3. Data Collection

Daily precipitation records were collected from three weather stations administered by the National Oceanic and Atmospheric Administration (NOAA), including LA Winnfield 3 N (ID: USC00169803), LA Jonesboro 4 ENE (ID: USC00164732) and LA Columbia Lock (ID: USC00161979) during 1978-2008 (Figure 2.1). Monthly and annual precipitation for each station was calculated separately first, then the averages from the three stations were used to represent the precipitation level in the studied region for further analysis.

Daily river discharge data were obtained for the study period from the United States Geological Survey (USGS) at the station of Little River near Rochelle, LA (USGS station No.: 07372200). Water quality data were obtained for the same time period from the Louisiana Department of Environmental Quality (LDEQ) for the Little River south of Rogers (LDEQ site No. LA081602_00) (Figure 2.1). Water quality data were collected on a monthly basis, including a variety of field and laboratory parameters. Total suspended solids (TSS), total Kjeldahl nitrogen (TKN, the sum of organic nitrogen and ammonia nitrogen), nitrate plus nitrite nitrogen (NO_3NO_2-N), and total phosphorus (TP) were used in this study. Although discharge data and water quality data were not measured at the exact same location, there was no major input or output between the USGS and LDEQ sites; therefore, the discharge at the USGS site was used to

compute nutrient and sediment mass loading using the LDEQ's water quality data. Details in methods for field sample collections and laboratory analysis can be found in LDEQ's Quality Assurance Project Plan for the Ambient Water Quality Monitoring Network (LDEQ, 2014).

2.2.4. Data Analysis

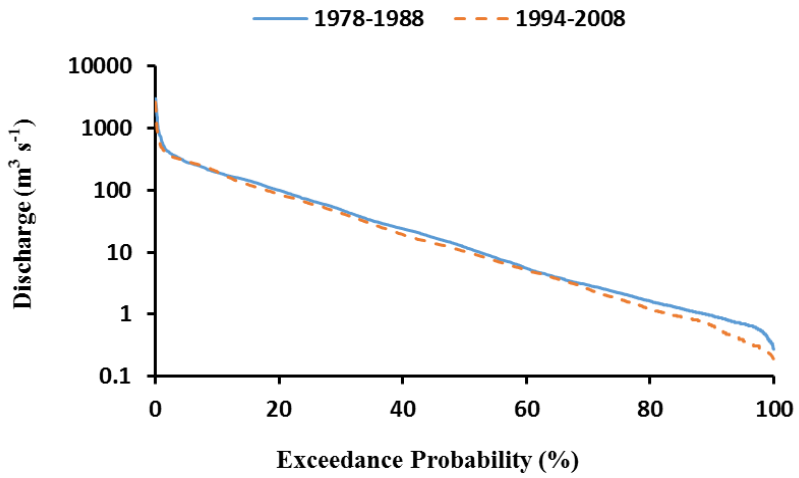

Figure 2.2 Daily flow duration curves of the Little River during 1978-1988 and 1994-2008.

The relationship between the frequency and magnitude of daily streamflow was depicted through the Weibull plotting position formula, which has been adopted as the standard plotting position method by the U.S. Water Resources Council in 1981 (Water Resources Council, 1981). This method plots the full range of streamflow conditions measured at a monitoring location against the probability of exceeding a given flow rate for a given time period (Vogel and Fennessey, 1995). In this study the exceedance probability was separately calculated for the two periods (before and after the wide implementation of forestry BMPs). All data used for calculation were based on measured daily discharge (in $m^3 \cdot s^{-1}$) from the USGS station. In the generated flow duration curves (FDC, Figure 2.2), flow conditions were classified as "High Flows," "Moist Conditions," "Mid-range Flows," "Dry Conditions," and "Low Flows," which corresponded to exceedance probabilities less than 10%, 10 - 40%, 40 - 60%, 60 – 90%, and

greater than 90%, respectively. All parameters of interest collected from the LDEQ site were across all five flow conditions and in an equal manner for both the pre-regulation and post-regulation periods.

Studies have found a close positive relationship of riverine TSS, TKN, NO_3NO_2-N and TP loads with the river discharge. The general log-linear regression model can be described in an equation as below (Xu, 2013; Joshi and Xu, 2015):

$$\ln(Si(t)) = b_0 + b_1 \ln(Q_{day}(t)) + \varepsilon(t) \quad (2.1)$$

where Q_{day} represents daily discharge in liters, $Si(t)$ represents daily loads in grams, *i* is the type of element, and *ε(t)* is an error term assumed to be normally distributed. In order to adjust the change caused by the application of BMPs, rating curves were developed for each element (i.e. TSS, TKN, NO_3NO_2-N, and TP) and separately for the pre-BMP implementation period (1978-1988) and the post-BMP implementation period (1994-2008). The potential log-biasing in the transformation procedure was checked by the correction factor (CF) given by Duan (1983) and modified by Gray et al. (2015):

$$CF = \frac{\sum_{i=1}^{n} Exp\ (ei)}{n} \quad (2.2)$$

where e_i is the difference between i^{th} field observations and model estimates, and *n* is the total number of samples used in the given rating curve. The fitted parameters and the statistical measures of fitness are summarized in Table 2.1. However, since the application of the CF didn't result in better estimates (Table 2.1) and due to the previous arguments regarding the reliability of the correction factors (Khaleghi et al., 2015), CF was not used in this study for loads estimates.

Long-term monthly river discharge and monthly concentrations of TSS, TKN, NO_3NO_2-N and TP were calculated based on the field measurements from USGS and LDEQ. Daily mass

transports of TSS, TKN, NO_3NO_2-N and TP during "High Flows" conditions and annual mass transports of all four parameters were estimated based on equation 1. In this study if more than 15 days data (any 15 days) were missing in a year, calculations of the total mass transport for that particular year would be considered invalid and excluded from the results (5 years were removed). Annual nitrogen to phosphorus molar ratios were also calculated based on mass transports of total nitrogen (TN, the sum of NO_3NO_2-N and TKN) and TP to understand possible changes in nutrient sources.

Table 2.1. Best fitting parameter estimates (b_0 and b_1) used in Eq. (2.1) for mass transport calculation of total suspended solids (TSS), total Kjeldahl nitrogen (TKN), nitrate and nitrite nitrogen (NO_3NO_2-N) and total phosphorus (TP), and their regression coefficients (R^2), sampling size (n) and root of mean square error (RMSE). "RMSE-CF" represents that the Duan correction factor (CF) is used during the retransformation procedure, while "RMSE-No CF" represents that the correction factor is not applied in the retransformation.

		b_0	b_1	R-squared	n	CF	RMSE-CF	RMSE-No CF
1978-1988	TSS	-3.495	0.993	0.88	105	1.366	4.839	0.708
	TKN	-6.563	0.978	0.96	110	1.078	3.866	0.393
	NO_3NO_2-N	-10.303	1.038	0.81	123	1.632	4.309	0.985
	TP	-6.360	0.865	0.91	111	1.140	3.654	0.532
1994-2008	TSS	-4.966	1.049	0.90	43	1.245	4.607	0.719
	TKN	-7.602	1.025	0.90	43	2.043	3.873	0.715
	NO_3NO_2-N	-9.660	1.014	0.82	31	1.500	4.423	0.940
	TP	-10.117	1.042	0.92	41	1.262	3.666	0.625

The Student's *t*-test was used to determine statistically significant differences between 1978-1988 and 1994-2008 on long-term annual and seasonal precipitation and river discharge. A one-way analysis of covariance (ANCOVA) was conducted to compare the effectiveness of forestry BMPs on TSS, TKN, NO_3NO_2-N and TP concentrations and loads whilst controlling for precipitation and

river discharge. Specifically, for annual and seasonal concentrations, the covariate was river discharge; for annual and seasonal loads, daily mass transports during "High Flows" conditions and TN/TP ratios, the covariate was precipitation. Levene's test and normality checks were carried out to make sure that assumptions were met. For all presented results, except for *p* values, standard errors and 95% confidence intervals were also provided as evidence for a difference (Nuzzo, 2014; Sterne and Smith, 2001).

The Mann–Kendall trend model was used to detect trends in the time series of the annual values of TSS, TKN, NO_3NO_2-N and TP concentrations for both pre-regulation and post-regulation periods (Kendall, 1975; Mann, 1945), which is derived statistically as:

$$S = \sum_{k=1}^{n-1} \sum_{j=k+1}^{n} \operatorname{sgn}(x_j - x_k) \tag{2.3}$$

$$\operatorname{sgn}(X_j - X_k) = \begin{cases} 1, & if\ X_j - X_k > 0 \\ 0, & if\ X_j - X_k = 0 \\ -1, & if\ X_j - X_k < 0 \end{cases} \tag{2.4}$$

where *S* is the Mann-Kendall test value, x_j and x_k are the annual median values in years *j* and *k*, *j* > *k*, respectively. Annual median values instead of mean value were used for calculation to avoid the disturbance from any outliers that may be caused by dilution effect of river discharges.

The Mann–Kendall test was to find the positive (increasing) or negative (decreasing) trends in concentrations of TSS, TKN, NO_3NO_2-N and TP. To estimate the true slope of an existing trend, the Sen's nonparametric method (1968) was used, which was calculated as:

$$f(t) = Qt + B \tag{2.5}$$

where Q is the slope and B is a constant. Q is calculated as:

$$Q_i = \frac{X_j - X_k}{j - k} \tag{2.6}$$

in the given Eq. (2.6), i = 1, 2, 3, …, N, whereas, at time *j* and *k* (j > k), *Xj* and *Xk* are the values of data pairs, respectively. The median of those N values of *Qi* is Sen's estimator, given as:

$$Q_{med} = \begin{cases} Q_{[N\ +\ 1]/2}, & if N\ is\ \text{odd} \\ \dfrac{Q_{[N/2]} + Q_{[N+2]/2}}{2}, & if\ N\ is\ even \end{cases} \quad (2.7)$$

All analyses were performed with the SAS Statistical Software package (SAS, 1996).

2.3. RESULTS

2.3.1. Precipitation and River Hydrological Conditions

Annual precipitation ranged from 960 to 1,872 mm with an average of 1,450 mm during the 1978-1988 period, and fluctuated from 1,004 to 1,724 mm with an average of 1,410 mm during the 1994-2008 period (Figure 2.3 above). In general, the interannual variation in precipitation during these two periods seemed to be very similar (p = 0.69). Long-term monthly average precipitation had similar trends for both periods, which decreased from early spring to late summer and then increased in subsequent months until the end of a year (Figure 3 below). Long-term monthly average precipitation fluctuated from 83 to 173 mm and from 84 to 147 mm during 1978-1988 and 1994-2008, respectively. Precipitation was relatively lower in May and from October to December during 1994-2008 compared to 1978-1988 (Figure 2.3 below). However, no significant difference was found between the two periods for monthly precipitation (p = 0.52).

During the period from 1978 to 1988, annual discharge of the Little River averaged 67 $m^3 \cdot s^{-1}$, ranging between 0.27 and 3,002 $m^3 \cdot s^{-1}$. From 1994 to 2008, the river had an average annual discharge of 61 $m^3 \cdot s^{-1}$, varying from 0.19 to 2,144 $m^3 \cdot s^{-1}$. Overall, the variation of discharge seemed to have decreased after the full implementation of forestry BMPs, especially in the 2000s (Figure 2.4a). Seasonally, the Little River had high flows in the winter months with its highest in February, and low flows in the summer months with the lowest in August for both periods (Figure 2.4b). Long-term monthly average discharge varied from 3 to 141 $m^3 \cdot s^{-1}$ during

1978-1988 and from 2 to 149 $m^3 \cdot s^{-1}$ during 1994-2008 (Figure 2.4b). Similar to the long-term seasonal precipitation, a decrease in average monthly discharge could be found in May and during October - December in 1994-2008 compared to 1978-1988. However, no significant difference was found in the long-term annual discharge (p = 0.66) and in the monthly average discharge (p = 0.75) between the two periods.

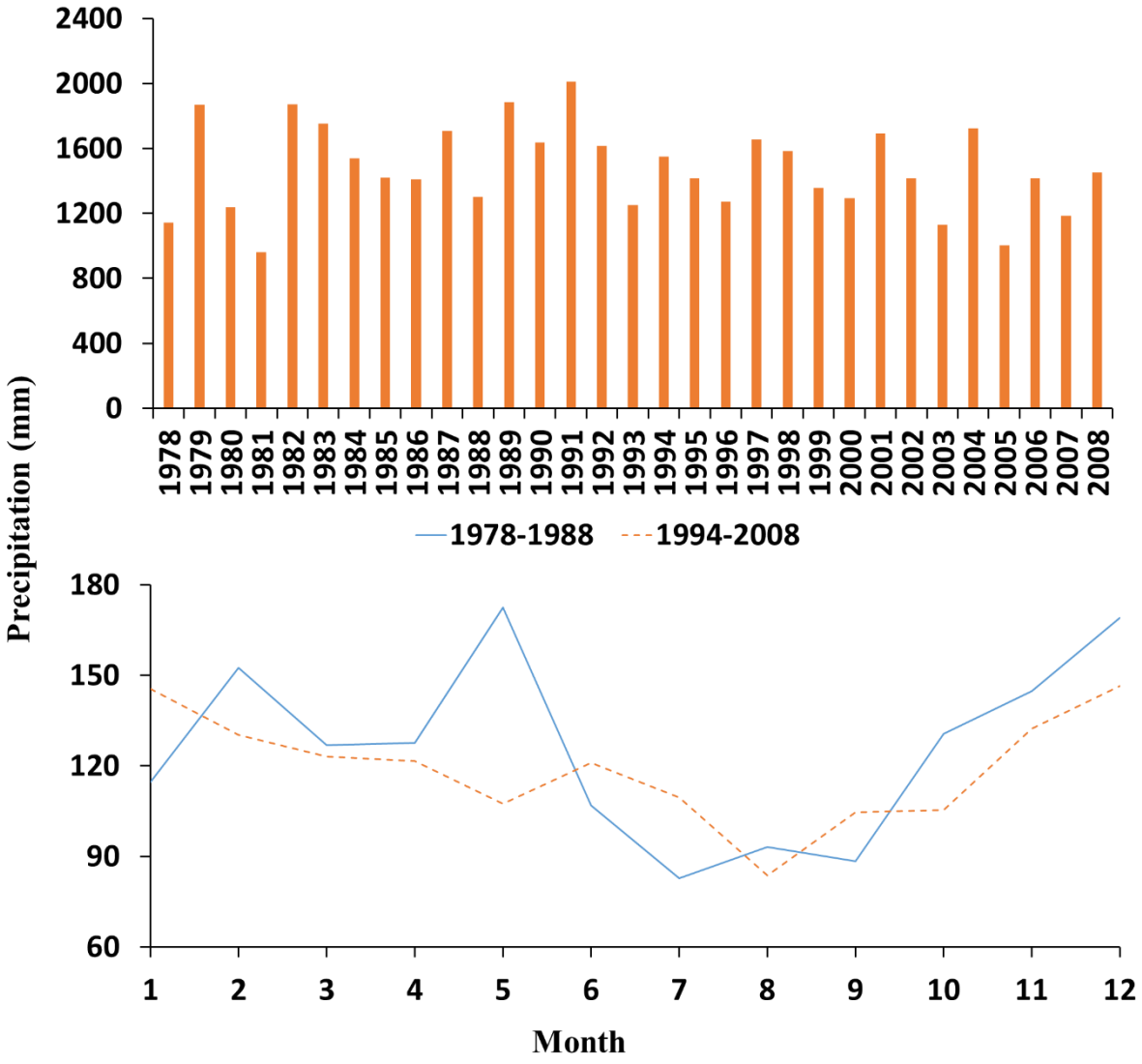

Figure 2.3. Long term annual (above) and monthly average precipitation (below) in the Little River Basin.

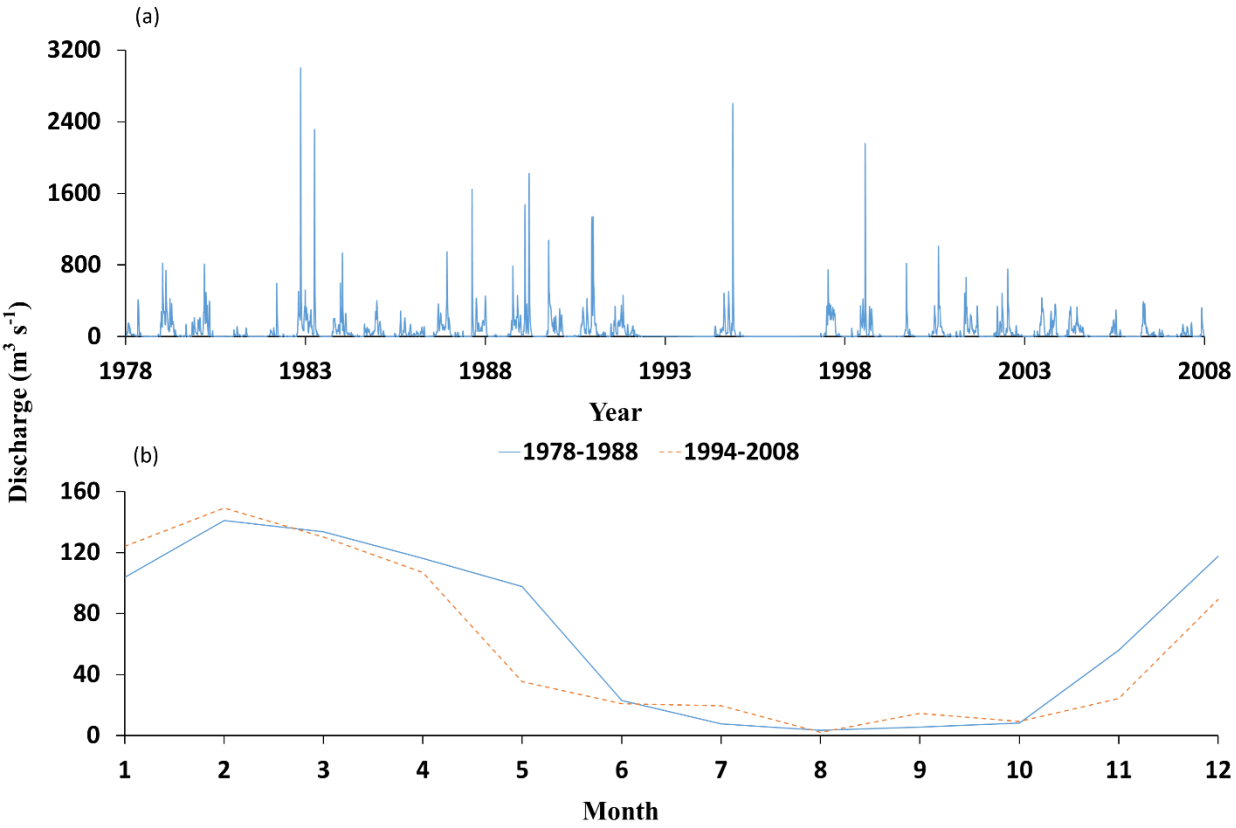

Figure 2.4. Long term annual (above) and monthly average discharge (below) of the Little River.

2.3.2. Long-term Annual Concentrations and Loads

After controlling for discharge, average long-term annual TSS concentration in the river significantly decreased from 34 to 25 mg L^{-1} after the wide implementation of BMPs (p = 0.038, Table 2.2). In general, measured TSS concentrations fluctuated from 2 to 122 mg L^{-1} during 1978-1988 and from 2 to 158 mg L^{-1} during 1994-2008. Specifically, annual TSS concentrations varied largely during the pre-BMPs period and seemed to be more stable during the 1990s. However, the variation of annual TSS concentrations seemed to increase again in the 2000s (Figure 2.5a). Annual TSS loads ranged from 8,690 to 109,000 metric tons (t) with a mean of 55,000 t in pre-BMPs period and from 18,000 to 65,000 t averaging 36,700 t in the post-BMPs period. The variations of TSS loads were similar to those of discharge (Figure 2.4a and 2.6a) with relatively less fluctuation during 1994-2008. There was a significant difference before and

after the use of BMPs in terms of annual TSS loads whilst controlling for precipitation (p = 0.024, Table 2.3).

Table 2.2. Average annual concentrations (in mg L^{-1}) and standard deviations (SD) of total suspended solids (TSS), total Kjeldahl nitrogen (TKN), nitrate and nitrite nitrogen (NO_3NO_2-N), and total phosphorus (TP) of the Little River during 1978-1988 and 1994-2008, and the statistics of a one-way analysis of covariance (ANCOVA), including adjusted mean, standard errors (SE) and 95% confidence interval, for each parameter controlling for discharge between the two periods. All data in the table are calculated based on field measurements.

			ANCOVA*			
	Concentration	Mean ± SD	Adjusted mean	SE	95% confidence interval	
					Lower bound	Upper bound
1978-1988	TSS	34 ± 8	34[a]	2.3	29	39
	TKN	0.97 ± 0.18	0.97[a]	0.05	0.87	1.08
	NO_3NO_2-N	0.12 ± 0.04	0.12[a]	0.02	0.08	0.15
	TP	0.12 ± 0.04	0.12[a]	0.01	0.10	0.15
1994-2008	TSS	25 ± 7	25[b]	2.9	19	31
	TKN	1.04 ± 0.15	1.00[a]	0.07	0.87	1.15
	NO_3NO_2-N	0.12 ± 0.07	0.13[a]	0.02	0.08	0.18
	TP	0.11 ± 0.03	0.11[a]	0.01	0.08	0.14

* For each parameter, adjusted means followed by the same letter within a column are not significantly different at the 0.05 level

Unlike TSS, annual TKN concentrations fluctuated throughout both the pre-regulation and post-regulation periods with less variability in 2006-2008 (Figure 2.5b). TKN concentrations averaged 0.97 mg L^{-1}, ranging from 0.27 to 3.59 mg L^{-1} before the implementation of BMPs, and averaged 1.04 mg L^{-1} varying from 0.02 to 2.32 mg L^{-1} in the twenty years afterwards. There was no significant difference found in TKN concentration after controlling for discharge between these two periods (p = 0.68, Table 2.2). Long-term TKN loads highly corresponded with discharge (Figure 2.4a, 2.6b). Large variation can be found in annual TKN loads: from 292 to 3,540 t $year^{-1}$ during 1978-1988 averaged 1,790 t and from 751 to 2,660 t $year^{-1}$ during 1994-2008 averaged 1,600 t. After controlling for precipitation, there was no significant difference between these two periods neither in TKN loads (p = 0.88, Table 2.3).

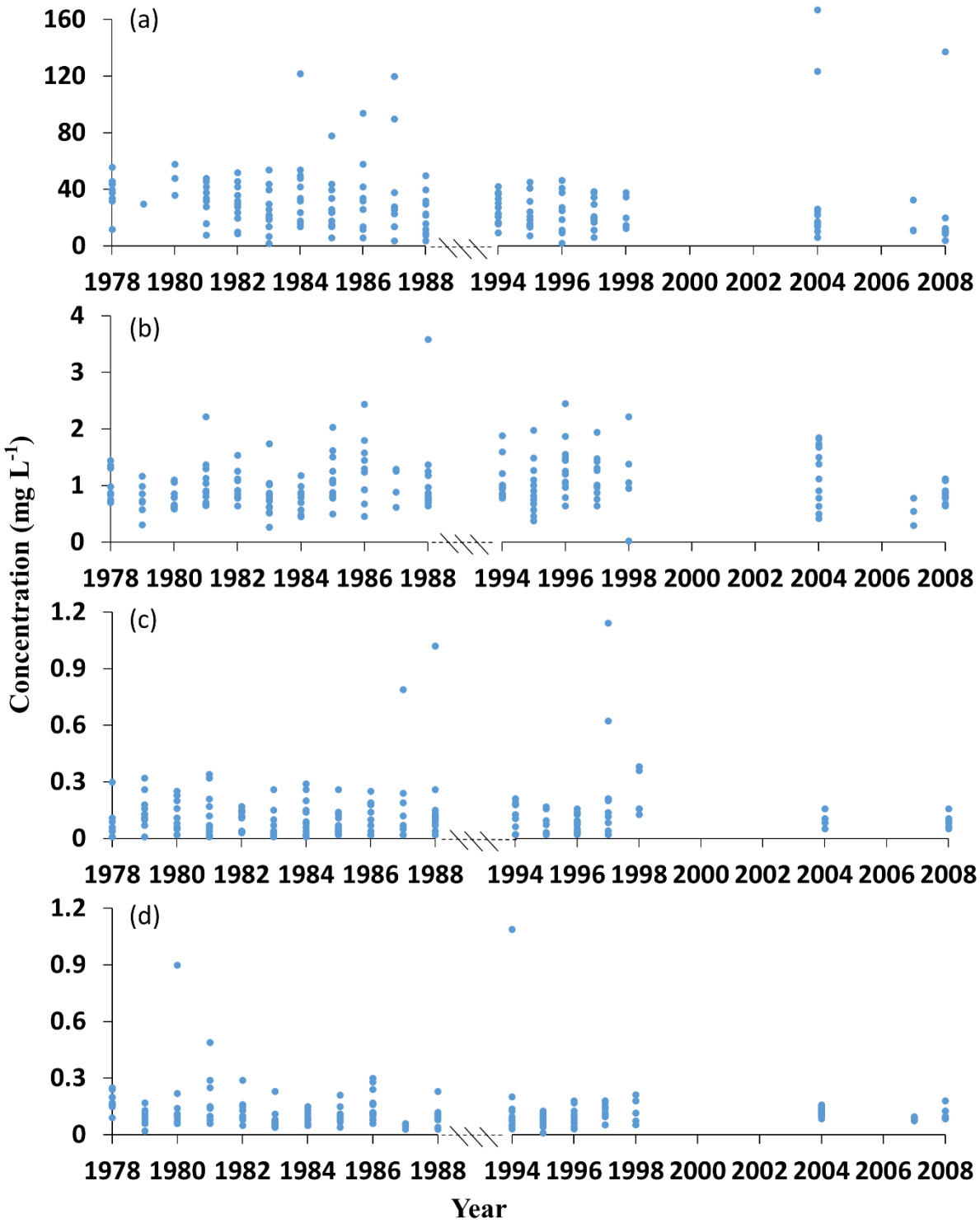

Figure 2.5. Measured concentrations of (a) total suspended solids, (b) total Kjeldahl nitrogen, (c) nitrate and nitrite nitrogen, and (d) total phosphorus in the Little River during the studied period. All measurements in each year are plotted as dots.

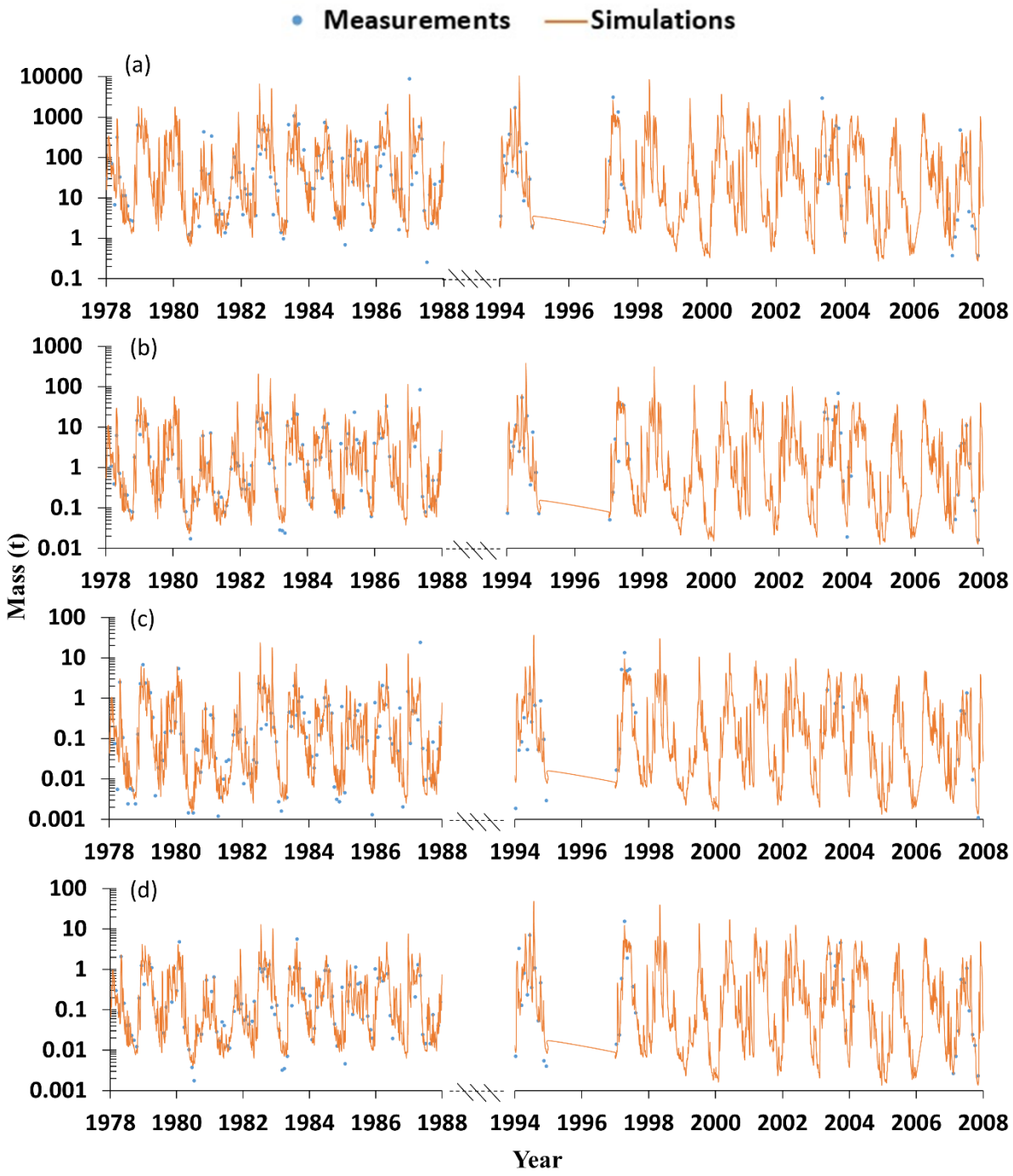

Figure 2.6. Long-term annual loads of (a) total suspended solids, (b) total Kjeldahl nitrogen, (c) nitrate and nitrite nitrogen, and (d) total phosphorus of the Little River during 1978-2008. Lines represent simulations estimated through Eq. (2.1), and dots are field measurements.

Long-term NO_3NO_2-N concentrations showed less variation in annual concentrations with few exceptions (Figure 2.5c). In the pre-BMPs period, measured NO_3NO_2-N concentrations averaged 0.12 mg L^{-1} fluctuating from 0.01 to 1.02 mg L^{-1}. In contrast, starting from 1994,

NO_3NO_2-N concentrations varied from 0.02 to 1.08 mg L^{-1} averaging at 0.12 mg L^{-1}. Annual loads of NO_3NO_2-N averaged 176 t (from 25 to 358 t) and 158 t (from 74 to 262 t) during 1978-1988 and 1994-2008, respectively. The trend of NO_3NO_2-N loads closely corresponded to annual discharge as well (Figure 2.4a, 2.6c). No statistically significant differences between these two periods were found in loads while controlling for precipitation (p = 0.94, Table 2.3) nor in annual concentration while controlling for discharge (p = 0.57, Table 2.2).

Table 2.3. Average annual mass transport (in metric ton) and standard deviations (SD) of total suspended solids (TSS), total Kjeldahl nitrogen (TKN), nitrate and nitrite nitrogen (NO_3NO_2-N) and total phosphorus (TP), and long-term annual TN/TP molar ratios for the Little River during 1978-1988 and 1994-2008. All parameters are compared for statistically significant differences between the two periods through a one-way analysis of covariance (ANCOVA) controlling for precipitation. All data in the table are derived from simulations by Eq. (2.1).

	Loads	Mean ± SD	ANCOVA* Adjusted mean	SE	95% confidence interval Lower bound	Upper bound
1978-1988	TSS	55,000 ± 27,200	53,900[a]	4,940	43,600	64,200
	TKN	1,790 ± 876	1,710[a]	154	1,390	2,030
	NO_3NO_2-N	176 ± 89.9	168[a]	15.4	135	200
	TP	152 ± 67.5	144[a]	15.9	111	178
	TN:TP	28 ± 2.4	28[a]	0.41	27	29
1994-2008	TSS	36,700 ± 17,400	37,600[b]	4,550	28,100	47,100
	TKN	1,600 ± 691	1,680[a]	154	1,360	2,000
	NO_3NO_2-N	158 ± 68.0	166[a]	15.4	134	198
	TP	192 ± 84.2	200[b]	15.9	167	233
	TN:TP	20 ± 0.2	21[b]	0.41	19	21

***** For each parameter, adjusted means followed by the same letter within a column are not significantly different at the 0.05 level

Similar to NO_3NO_2-N, except for a few measurements, long-term annual TP concentrations had relatively small variations for both 1978-1988 and 1994-2008 (Figure 2.5d). Average annual TP concentrations ranged from 0.02 to 0.90 mg L^{-1} before 1988 and from 0.01 to 1.03 mg L^{-1} since 1994 in the studied period. After controlling for discharge, no significant difference in annual TP concentration (p = 0.50, Table 2.2) can be found between pre-BMPs (averaged 0.12 mg L^{-1}) and post-BMPs periods (averaged 0.11 mg L^{-1}). Like other nutrients, TP loads had a similar trend to the discharge (Figure 2.4a, 2.6d), and there was a significant difference between 1978-1988 and 1994-2008 after controlling for precipitation (p = 0.024, Table 2.3). Annual loads of TP varied from 31 to 280 t, averaging 152 t in pre-BMPs period, while post BMPs period loads ranged from 90 to 320 t averaging 192 t.

After controlling for precipitation, the TN/TP ratio decreased significantly from 28 to 21 after the wide implementation of forestry BMPs (p < 0.01, Table 2.3). Also, interannual TN/TP ratios were much less variable during 1994-2008.

2.3.3. Long-term Seasonal Concentrations and Loads

Average monthly TSS concentrations ranged from 23 to 43 mg L^{-1} and 12 to 56 mg L^{-1} for 1978-1988 and 1994-2008, respectively. The seasonal trends of long-term monthly TSS concentrations for the two periods were similar, both of which decreased from highs in February to lows in early summer, increased to relatively high levels in fall, and then decreased in December and was low until the next peak (Figure 2.7a). However, it was also obvious that the seasonal variation was greater after extensive BMPs implementation. Nine out of twelve months showed an equal or decreased long-term monthly TSS concentrations during 1994-2008 compared to the pre-BMPs period (Figure 2.7a). Specifically, average monthly TSS concentrations were significantly lower from March to June (p = 0.01, Table 2.4) and from

September to December ($p < 0.01$, Table 2.4) after controlling for discharge. However, no year-round significant difference was found between the two periods in long-term seasonal trends of TSS concentration ($p = 0.14$).

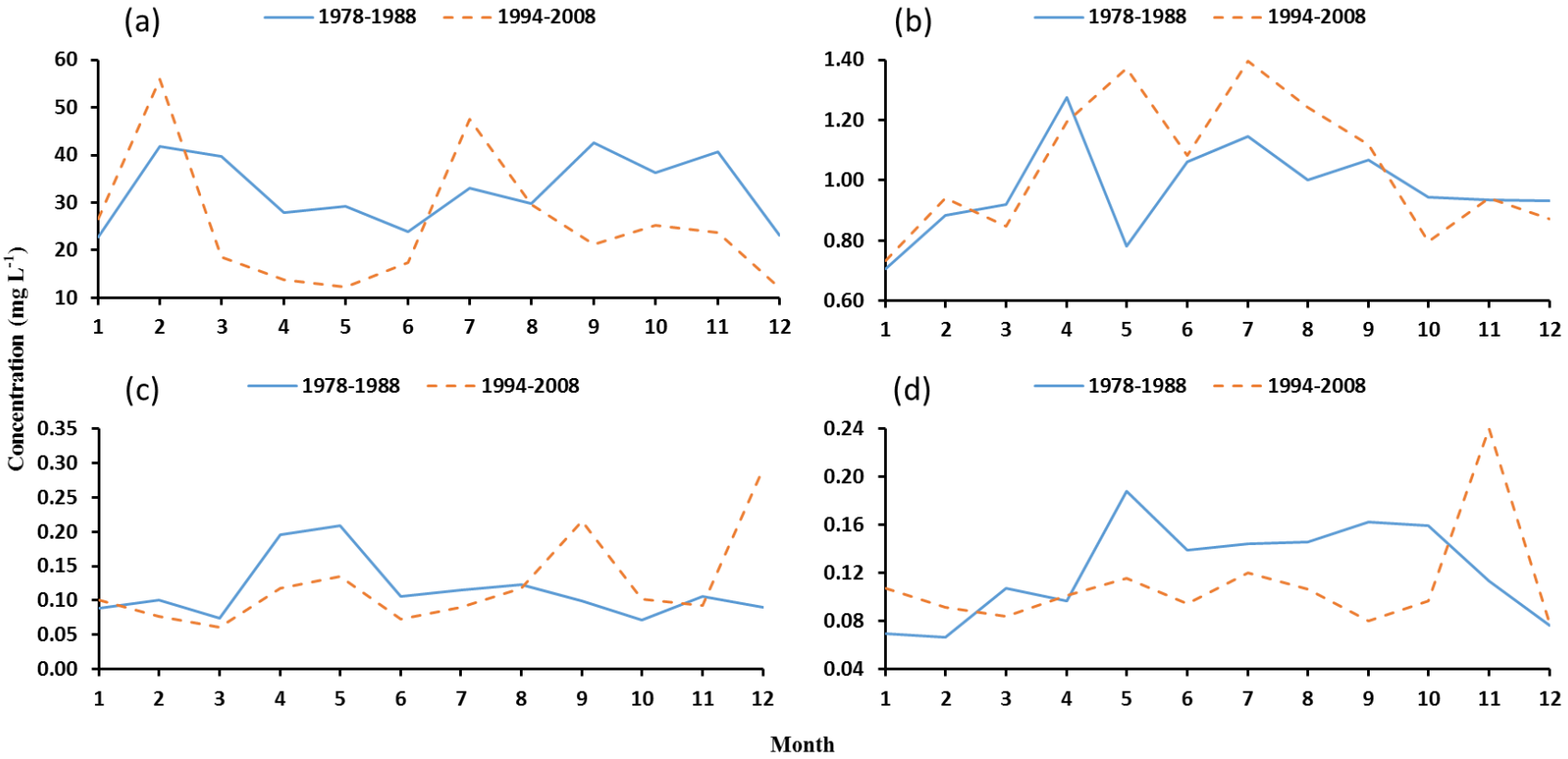

Figure 2.7. Long-term average monthly concentrations of (a) total suspended solids, (b) total Kjeldahl nitrogen, (c) nitrate and nitrite nitrogen, and (d) total phosphorus of the Little River during 1978-1988 and 1994-2008.

Average monthly TKN concentrations changed from 0.71 to 1.28 mg L^{-1} and from 0.73 to 1.40 mg L^{-1} before and after extensive implementation of BMPs, respectively. Like TSS, fluctuations of seasonal trends for the two periods were similar, during both of which TKN increased in spring, went down in early summer, went up again in the fall and decreased in winter (Figure 2.7b). Five out of twelve months had an equal or lower measurement of TKN concentration. After controlling for discharge, there was no statistical difference between the pre-regulation and post-regulation periods in terms of long-term monthly TKN concentration (p = 0.41).

Table 2.4. Statistics of a one-way analysis of covariance (ANCOVA), including adjusted mean, standard errors (SE) and 95% confidence interval, for average monthly concentrations of parameters of interest controlling for discharge between the 1978-1988 period and the 1994-2008 period. Only the parameters and months with significant differences are presented. All data in the table are calculated based on field measurements.

		Month	Mean ± SD	ANCOVA*			
				Adjusted mean	SE	95% confidence interval	
						Lower bound	Upper bound
1978-1988	TSS	Mar-Jun	30 ± 7	30[a]	2.36	24	36
		Sep-Dec	36 ± 9	37[a]	2.14	31	42
	TP	Mar-Oct	0.14 ± 0.03	0.14[a]	0.008	0.13	0.16
1994-2008	TSS	Mar-Jun	16 ± 3	16[b]	2.36	10	22
		Sep-Dec	21 ± 6	20[b]	2.14	14	25
	TP	Mar-Oct	0.10 ± 0.01	0.10[b]	0.008	0.08	0.12

* For each parameter, adjusted means followed by the same letter within a column are not significantly different at the 0.05 level

Average monthly NO_3NO_2-N concentrations fluctuated from 0.07 to 0.21 mg L^{-1} before 1988 and from 0.06 to 0.29 mg L^{-1} since 1994. Seasonal trends for long-term monthly NO_3NO_2-N concentration were similar to each other as well for two studied periods (Figure 2.7c). For eight months of a year, long-term monthly NO_3NO_2-N concentrations were lower after BMPs.

However, no significant difference was observed in long-term monthly NO_3NO_2-N concentrations whilst controlling for discharge between the two periods. ($p = 0.76$).

In 1978-1988, average monthly TP concentrations varied from 0.07 to 0.19 mg L^{-1} while in 1994-2008 they varied from 0.08 to 0.24 mg L^{-1}. In 1978-1988, long-term monthly TP concentrations seemed to be lower in winter months and higher in summer months. In comparison, long-term average TP concentrations during 1994-2008 didn't show a clear seasonal trend besides a pulse in November (Figure 2.7d). After the extensive implementation of BMPs, lower long-term monthly TP concentrations were observed nine months out of the year. Specifically, average monthly TP concentrations in 1994-2008 were significantly lower from May to October after controlling for discharge ($p < 0.01$, Table 2.4). However, there was no significant difference between pre-BMPs and post-BMPs periods for long-term year-round TP concentrations ($p = 0.31$).

Long-term monthly loads of TSS, TKN, NO_3NO_2-N nitrogen and TP in the Little River showed a seasonal trend closely correlated to river discharge (Figure 2.4b, Figure 2.8). From 1978 to 1988, average amounts of monthly TSS, TKN, NO_3NO_2-N, and TP from the Little River to Catahoula Lake ranged from 244 to 9,240 t, from 8 to 301 t, from 1 to 30 t and from 1 to 25 t, respectively. In comparison, during 1994 to 2008 the mean amounts of monthly TSS, TKN, NO_3NO_2-N, and TP entering Catahoula Lake varied from 101 to 8,050 t, from 5 to 326 t, from 0.5 to 32 t, from 1 to 40 t, respectively. In general, after extensive implementation of forestry BMPs, long-term monthly loads seemed to be lower for TSS, higher for TP, and relatively the same for nitrogen, which was most evident during months with greater discharge in winter and spring (Figure 2.8). No significant difference was found for long-term seasonal loads of TSS,

TKN, NO_3NO_2-N, and TP after controlling for precipitation (p = 0.65, 0.73, 0.74, 0.14, respectively).

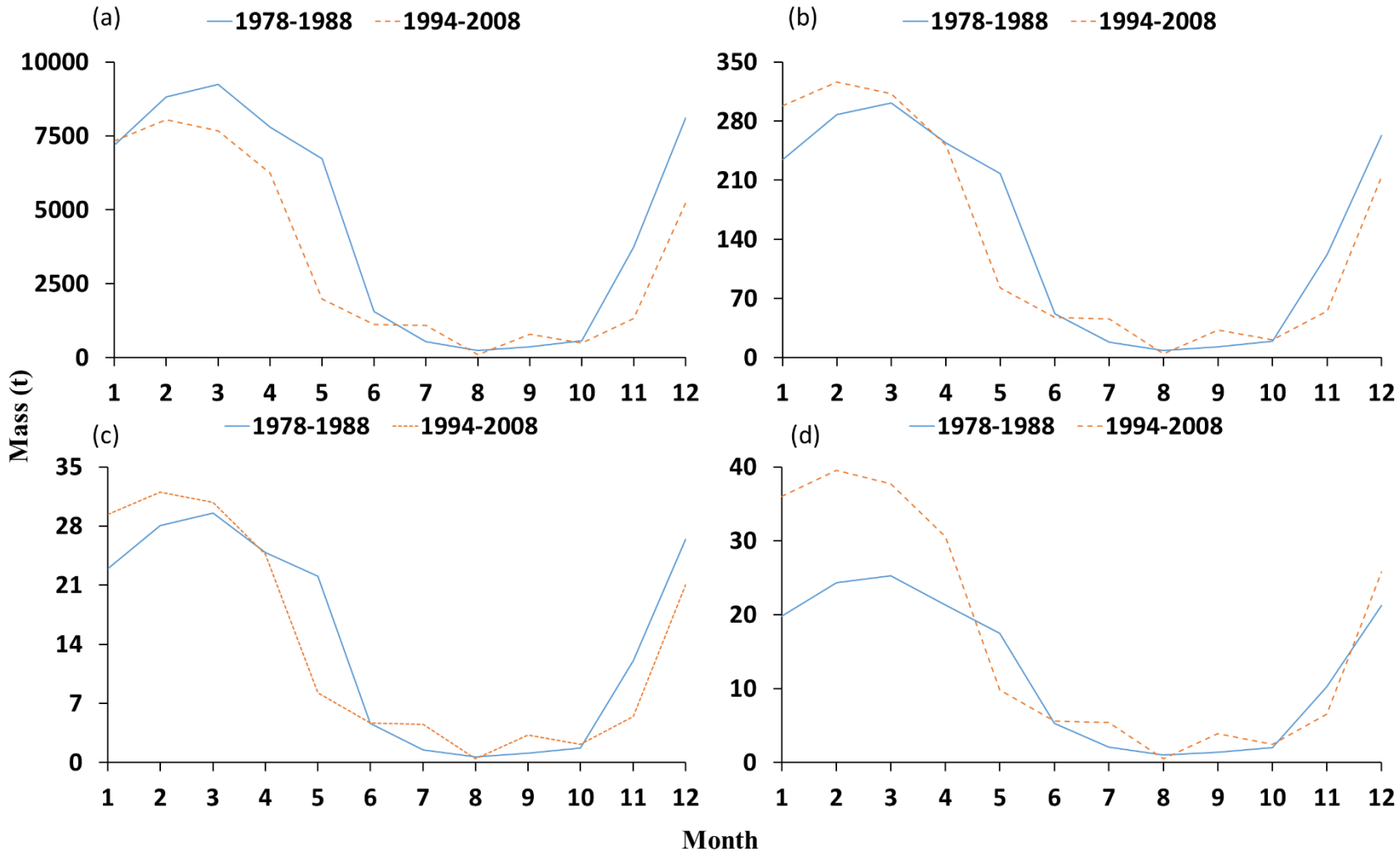

Figure 2.8. Long-term average monthly mass transports of (a) total suspended solids, (b) total Kjeldahl nitrogen, (c) nitrate and nitrite nitrogen, and (d) total phosphorus from the Little River during 1978-1988 and 1994-2008.

2.3.4. Streamflow Frequency and Magnitude

Flow duration curves (FDC) of the daily discharge generated from the two studied periods were very similar (Figure 2.2). Based on FDCs, daily discharge that was greater than 195 and 196 $m^3 \cdot s^{-1}$ could be considered as "High Flows" for 1978-1988 and 1994-2008, respectively (Figure 2.2). During "High Flows" conditions, average daily loads of TSS were decreased from 877 to 702 t after the extensive implementation of forestry BMPs, whilst controlling for precipitation ($p < 0.01$, Table 2.5). In comparison, no significant differences were found for average daily TKN ($p = 0.94$, Table 2.5) and NO_3NO_2-N ($p = 0.37$, Table 2.5) loads during 1994-2008. Contrary to TSS, significant increases were found for average daily TP loads since 1994 after controlling for precipitation (from 2.2 t in 1978-2008 to 3.4 t in 1994-2008, $p < 0.01$, Table 2.5).

Table 2.5. Average daily mass transport (in metric ton) and standard deviations (SD) of total suspended solids (TSS), total Kjeldahl nitrogen (TKN), nitrate and nitrite nitrogen (N NO_3NO_2-N) and total phosphorus (TP) during high flow conditions, and the statistics of a one-way analysis of covariance (ANCOVA), including adjusted mean, standard errors (SE) and 95% confidence interval, for each parameter controlling for daily precipitation. High flow was considered to be any average daily discharge (m^3 s^{-1}) with an exceedance probability less than 10 %.

	Loads	Mean ± SD	ANCOVA*			
			Adjusted mean	SE	95% confidence interval	
					Lower bound	Upper bound
1978-1988	TSS	878 ± 768	877[a]	34.1	810	944
	TKN	28.3 ± 24.1	28.3[a]	1.17	26.0	30.6
	NO_3NO_2-N	2.9 ± 2.7	2.9[a]	0.12	2.66	3.14
	TP	2.2 ± 1.5	2.2[a]	0.12	1.94	2.39
1994-2008	TSS	700 ± 582	702[b]	32.6	638	766
	TKN	28.1 ± 22.4	28.1[a]	1.12	25.9	30.3
	NO_3NO_2-N	2.7 ± 2.1	2.8[a]	0.12	2.52	2.98
	TP	3.4 ± 2.8	3.4[b]	0.11	3.21	3.65

* For each parameter, adjusted means followed by the same letter within a column are not significantly different at the 0.05 level

2.3.5. Trend Analysis of Annual Median Concentrations

For TSS, TKN, NO_3NO_2-N and TP concentrations, Sen's slope estimates (*Q*) were -1.7, 0.023, 0.001, -0.005 for the 1978-1988 period, and were -0.838, 0.020, 0.004, 0.001 during the 1994-2008 period (Table 2.6). A significant decreasing trend was detected only in annual median concentrations of TSS in the post regulation period (1994-2008, $p < 0.05$, Table 2.6), while a less significant increasing trend was detected for annual median concentrations of TKN in the pre regulation period ($0.05 < p < 0.1$, Table 2.6). In comparison, no other significant trend was found based on the Mann–Kendall model. It's also worth noting that TP changed its annual trend from a decreasing direction during 1978-1988 to an increasing direction during 1994-2008, although neither of them was not statistically significant. Those results were in agreement with ANCOVA results calculated by annual average concentrations.

Table 2.6. Trend analysis with the Mann–Kendall model and Sen's slope estimation of annual median values for total suspended solids (TSS), total Kjeldahl nitrogen (TKN), nitrate and nitrite nitrogen (NO_3NO_2-N), and total phosphorus (TP).

		Trend	*p* value	Sen's slope estimation	
				Q	B
1978-1988	TSS	Decreasing	$p > 0.1$	-1.7	39.14
	TKN	Increasing	$0.05 < p < 0.1$	0.023	0.83
	NO_3NO_2-N	Increasing	$p > 0.1$	0.001	0.08
	TP	Decreasing	$p > 0.1$	-0.005	0.14
1994-2008	TSS	Decreasing	$p < 0.05$	-0.838	35.8
	TKN	Increasing	$p > 0.1$	0.020	0.58
	NO_3NO_2-N	Increasing	$p > 0.1$	0.004	-0.02
	TP	Increasing	$p > 0.1$	0.001	0.07

2.4. DISCUSSIONS

2.4.1. BMP Effectiveness on Sediment Runoff

The TSS reduction found in this study from 1994 to 2008 demonstrates that long-term BMPs have the capacity to mitigate impacts of forest operations on water quality regarding

surface erosion at a river basin scale. This fills the knowledge gap in the verification of the overall effects of forest activities on water quality in terms of sediment transport. In more detail, many previous studies have frequently cited forest road activities as one of the major contributors to surface soil runoff on forestlands, with the majority of investigations on soil erosion (Grace, 2005). In the Coastal Plain region, erosion rate studies have been conducted extensively as well (Beasley and Granillo, 1988; Blackburn et al., 1986; Grace, 2002). However, few of them have related observed erosion rates to the quantity of sediment delivered to water systems or water quality. Sediment delivery to forest streams does not necessarily mirror erosion losses observed upslope since downslope sediment trapping characteristics are also influential (Grace, 2005). Also, even though forested SMZs are considered effective in trapping sediment and reducing stream TSS concentrations (Cristan et al., 2016), very little effort has been made to assess the frequency of SMZ breakthroughs for the Coastal Plain region. In this case, this study provides direct evidence that BMPs have favorable impacts on the water that drains forests in terms of reducing sediment runoff, and those positive effects are especially profound during "High Flow" conditions.

Deciphering the relative importance of implemented forest operations leading to the reduction in sediment runoff is difficult due to the complex interactions of land use, landform, and disturbance. In general, BMPs implementation was very high for harvesting operations (96.4%) and site preparation treatments (95.8%) (Kaller, 2009), which may play a bigger role in surface erosion control since previous studies in the same region have reported significant increases in sediment concentrations in the water draining from areas affected by those treatments without BMP implementation (Beasley, 1979). In contrast, more attention may be needed for forest road construction and maintenance in the studied area, which has been

recognized as one of the primary risk areas in relation to sediment loss from forest management activities. According to the Louisiana Department of Agriculture and Forestry, road construction within SMZs had significantly lower BMP implementation (50%) than any other SMZ activity (Kaller, 2009). In addition, due to the flat watershed topography in Louisiana and the resulting sluggish stream flow, the effectiveness of BMP implementation may be aided since sediments could be stored within the stream channel through deposition.

Measured TSS concentrations in the Little River Basin are well within the range of other published data in the Coastal Plain region (Beasley and Granillo, 1988; Keim and Schoenholtz, 1999; Riekerk, 1982; Riekerk, 1983; Williams and Askew, 1998), and the result of this study is consistent with other publications regarding the long-term performance of BMPs on sediment reduction in other regions. Reiter et al. (2009) assessed long-term data on stream discharge, suspended sediment, and turbidity to determine impacts of sediment control practices (BMPs) on water quality over 30 years in the Pacific Northwest of Washington. The authors found that turbidity declined at all monitoring sites in their study. When evaluated for the entire watershed, turbidity levels still declined, even with continued active forest management. They concluded that declined sediment production was directly related to reducing sediment production from roads and minimizing the amount of road runoff reaching stream channels (Reiter et al., 2009). In another 15-year paired watershed study on the effects of BMPs on controlling nonpoint source pollution in the Ridge and Valley of central Pennsylvania, Lynch and Corbett (1990) found significant, however relatively small, increases at two years post-harvest in turbidity. They concluded that BMPs were effective due to no serious alterations of water quality.

2.4.2. BMP Effectiveness on Nutrient Runoff

2.4.2.1. Phosphorus

BMPs don't seem to have any discernible long-term effect on phosphorus concentrations at a basin scale in this study. Phosphorus, especially phosphate, is of concern because elevated concentrations can result in eutrophication of freshwater lakes. A phosphate concentration standard of 0.5 mg L^{-1} has been established to protect freshwater lakes (MacDonald et al., 1991). Changes in levels of phosphorus in forest streams are usually associated with the transport of soil particles carried by overland flow (Barling and Moore, 1994; Gravelle et al., 2009), and harvesting (Grace, 2005) and site preparation (Johnson et al., 1986) are often referenced with the potential to increase phosphorus concentrations. In this study, the long-term BMPs implementation seemed to be very effective in trapping sediments, especially during "High Flow" conditions. However, similar positive effects could not be found for TP. The TN:TP ratio analysis show a significant decrease during 1994-2008, indicating that possible external phosphorus sources may exist after the wide implementation of forestry BMPs. Therefore, effects of forestry BMPs in phosphorus control may be offset by other factors like fertilization.

Fertilization practices in the southern United States have been changing with an increased area of pine plantations being fertilized annually since 1991 (Fox et al., 2004; Fox et al., 2007). In the lower Coastal Plain and Gulf Coasts, poorly drained, clayey Ultisols tend to be severely phosphorus deficient (Fisher and Garbett, 1980). Along the Gulf Coast, well drained, clayey to loamy soils on the Citronelle and associated geological formations also have been found to be phosphorus deficient (Allen and Lein, 1998). Therefore, forest fertilization is usually included in silvicultural regimes to increase plantation growth (Allen, 1987). In the South, from 1978 to 1991 fertilized forested land increased around 80 ha $year^{-1}$, while beginning in 1991 the area of

fertilized forestland doubled approximately every 2 years through 1999 when fertilization peaked at 640,000 ha. Since 1999, fertilized forested land has averaged 570,000 ha $year^{-1}$ (Albaugh et al., 2007). As a result, before 1990 less than 80,000 ha of southern pine plantations were fertilized whereas over 500,000 ha were fertilized in 2004 (Forest Nutrition Cooperative, 2005). During this period, fertilizer applications were mainly for phosphorus fertilization which was added to at least 80% of the fertilized forestland in all but one year, aiming at solving the problems of insufficient phosphorus availability in soils for tree demand throughout the rotation and phosphorus deficiencies developed soon after the seedlings are planted (Albaugh et al., 2007, Fox et al., 2007; Pritchett and Comerford, 1982). Specifically, from 2000 to 2004, at least 80% of fertilized area in the South was in the Coastal Plain region with an average amount of 237,000 t fertilizer $year^{-1}$ applied to forests (Albaugh et al., 2007).

The effect of phosphorus fertilization would be mostly obvious during phosphorus exports in large or intense storm events. Results in this study have shown that during "High Flow" conditions, TP loadings were significantly increased by 55% in the post BMP implementation era (Table 2.5). It could be attributed to the reason that changes in TP concentrations and loads in forest waters are usually determined by the rapid addition of phosphorus during fertilization, and the slow movement of phosphorus into the stream over time from soils near the stream. Since flow duration curves for the two periods are similar, it is very likely that TP concentrations were higher during "High Flow" conditions after the increased use of phosphorus fertilizer. This may indicate that although forestry BMPs were significantly effective in TSS reduction, in large or intense storm events the offset effects from the fertilizer overwhelmed the effects of BMPs, leading to an increase in the TP concentration in the river. By contrast, in drier conditions, BMPs' significant effects in trapping sediments may dominate,

which could greatly reduce the movement of phosphorus and decrease the TP concentration in forest waters. As a result, TP loadings in 1994-2008 could increase with the average TP concentrations for the two periods being generally the same (Table 2.2 and 2.3) since phosphorus exports in large or intense storm events could account for the majority of the total TP mass transport. This could also be an explanation why average TP concentrations were lower from May to October (Figure 2.7d) and why monthly average TP loads were much greater from January to April in 1994-2008 (Figure 2.8d).

2.4.2.2. Nitrogen

Study findings indicate that the long-term effectiveness of nitrogen reduction is also limited at the basin scale. Some previous studies have claimed that harvesting and site preparation would typically lead to increased water yields, soil moisture, and solar radiation on the soil surface due to the removal of forest vegetation. As a result, nitrogen concentration, especially nitrate and nitrite, in forest waters may increase after timber harvest because of decreased plant uptake, increased flushing by shallow flow pathways, and increased soil temperatures that increase mineralization and nitrification rates (Martin et al., 1984; Marchman et al., 2015). Those conclusions are mostly derived from short-term studies, and may not be valid for long-term cases. Although some forestry studies have shown short-term increases in stream nitrogen levels after harvesting (e.g. Likens et al., 1970; Pardo et al., 1995), many other studies have noted that nitrogen exports returned to pre-harvest levels a few years after harvesting because of uptake by re-growing vegetation while soil nitrification returned to pre-disturbance rates (Edwards and Williard, 2010). The efficiency of nitrogen self-regulating mechanisms in forests over longer periods of time may explain why no change is found in nitrogen concentrations over the 30 year span of this basin scale study.

In addition, forestry BMPs are not developed to fundamentally control nitrogen transport through all mechanisms. Nitrogen, mainly nitrate and nitrite, is transported primarily through leaching of soluble species. Much of the TKN is also transported as dissolved organic nitrogen. Forestry BMPs are designed to control nitrogen transport mainly through minimizing the incidence of Horton overland flow moving from the harvesting areas to the streams, and SMZs are often considered as one of the most functional parts in BMPs that sequester nitrogen transport and promote denitrification (Lowrance et al., 2000). However, most forestry BMPs don't have the capacity to affect subsurface processes, except for encouraging infiltration of surface flows to the extent possible. Therefore, dissolved nutrients such as nitrate, which commonly travels by subsurface pathways, could not be substantially influenced by BMPs. This is demonstrated in this study by similar amounts of nitrogen mass transport during "High Flow" conditions between the two study periods (Table 2.5). Based on the discussion above, at basin scale it may be expected to see limited long-term effectiveness of forestry BMPs on nitrogen control.

2.4.2.3. Comparisons with other studies in the Southern/Southeastern Coastal Plain region

The nitrogen and phosphorus levels observed in this study are within the range of those reported from other publications for forest streams in the southern/southeastern Coastal Plain region. For instance, in a study of decadal nutrient inputs of coastal rivers, He and Xu (2015) reported similar ranges of annual concentrations for TKN, NO_3NO_2-N and TP in the past 30 years in Sabine River (0.52-1.49, 0.04-0.10 and 0.04-0.11 mg L^{-1}, respectively) and Calcasieu River (0.42-1.22, 0.07-0.24 and 0.06-0.16 mg L^{-1}, respectively) whose river basins are forest-pasture dominated (54% and 51%, respectively) in coastal Louisiana. In another study focusing on effects of forest harvesting and BMPs on nutrient concentrations in the Upper Coastal Plain,

authors observed median concentrations ranging from 0.01 to 0.05 mg L^{-1} for TP and from 0.44 to 2.89 mg L^{-1} for total nitrogen (TN) during pre-harvest period, and varying from 0.008 to 0.03 mg L^{-1} for TP and from 0.41 to 2.99 mg L^{-1} for TN in post-harvest period for all their monitoring sites in small headwater streams in southwest Georgia (Marchman et al., 2015).

Reported effectiveness of forestry BMPs in adjusting phosphorus and nitrogen levels in water draining from forested watersheds is variable for short-term and/or plot-scale cases in the Southern Coastal Plain region (Edwards and Williard, 2010; Marchman et al., 2015; Wynn et al., 2000). In comparison, very few studies have been conducted reporting long-term effectiveness of forestry BMPs at basin scale in terms of nutrient runoff (Cristan et al., 2016). Based on the discussion above taken collectively, we suggest more future studies to be taken to test the long-term effectiveness of forestry BMPs on nutrient runoff at a large watershed scale.

2.4.3. Strengths and Limitations of Long-term Watershed-scale BMP Evaluation

In plot-scale/short term studies, effectiveness of forestry BMPs may be overestimated or underestimated due to the types of flow conditions that occur during monitoring. For example, most suspended sediment transport occur during large or intense storm conditions (Beasley, 1979), which occur infrequently and randomly. Therefore, even if sediment is delivered to a channel and remains relatively available, it may not be flushed from the watershed during the period of stream water monitoring. This would result in an overestimate of the BMP efficiency because the temporary storage would be interpreted as better BMP effectiveness than actually occurred. In contrast, long-term watershed-scale studies could overcome this type of shortages to a great extent and better represent the collective effectiveness of forestry BMPs.

However, large watersheds tend to have myriad sinks that may delay or attenuate the solute signal from the land. For instance, some eroded sediment originating from management

activities may be stored on the hillside or in the channel. If the area of storage was a riparian buffer and if storage is permanent, then the attribution of the reduction of the constituent delivery is fully appropriate in the evaluation of the BMP effectiveness. If storage was not by the riparian buffer or it was not permanent, substantial amounts of sediment delivered to a stream channel can be stored for decades and perhaps longer before being flushed from the watershed (Trimble, 1981), leading to BMPs efficiencies being incorrectly evaluated in some situations. Additionally, there may be changes in the forestry equipment and approaches over a long period of time, some of which are hard to track and include in the statistical analysis. Therefore, it should be noted that limitations exist for the evaluation of long-term BMP effectiveness in a large watershed.

2.5. CONCLUSIONS

This study assessed long-term trends of total suspended solids, nitrate/nitrite nitrogen, total Kjeldahl nitrogen, and total phosphorus concentrations and loads in an intensively-managed forested watershed in the southern United States. The goal of the study was to examine the effectiveness of forestry BMPs in water quality protection at a basin scale and in a longer term. Based on the results, we conclude that forestry BMPs are effective in reducing sediment runoff from the intensively managed forested watershed. Although stream sediment loading was strongly reduced following BMP implementation, TP loading at the basin outlet increased by 27 %, which was probably caused by a drastic increase in the application of phosphorus fertilizer after 1991. Stream nitrogen concentrations and loading in the post BMP implementation era showed little change when compared to those in the pre-BMP implementation period. The results suggest that current BMP guidelines for fertilization and nutrient management need to be reviewed and improved. This study filled a knowledge gap in the long-term effectiveness of forestry BMPs at a basin scale in the southern Coastal Plain region of the United States. Since

forestry BMPs are region-specific, we suggest future studies be conducted in other regions at a large watershed scale.

CHAPTER 3. DISSOLVED CARBON TRANSPORT IN A RIVER-LAKE CONTINUUM: A CASE STUDY IN A SUBTROPICAL WATERSHED, USA

3.1. INTRODUCTION

Studying the biogeochemical connectivity between rivers and lakes can help us understand their ecological and environmental impacts within a drainage basin. Rivers are the principal linkages from the land to the ocean carrying suspended and dissolved materials, the transfer of which are key components of the carbon balance at the decadal to centennial scale, the sediment balance, the nutrient balance of surface waters, and control the coastal zone functioning to a great extent (Milliman et al., 1987; Wafar et al., 1989; Caddy and Bakkun, 1994; Meybeck, 2003; Gong et al., 2015). In a river-lake network, lakes have been found to remove nitrogen (Harrison et al., 2009) and carbon substantially (Cole et al., 2007; Bastviken et al., 2011). Nowadays lakes are increasingly being studied in the context of biogeochemical connectivity across waterscapes (Winter, 1999; Jones, 2010; Lottig et al., 2011; Lottig et al., 2013), which remains an emerging research frontier (Powers et al., 2014).

Carbon, required by all aquatic organisms, is one of the most concerned elements in aquatic geochemistry studies. Dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) together constitute the major carbon reservoir in rivers and lakes, which have been recognized as important components of the global carbon cycle interacting with atmospheric, terrestrial and oceanic carbon (Brunet et al., 2005; Shin et al., 2015). DIC is often the most abundant inorganic carbon phase in rivers and streams in aquatic ecosystems (Marx et al., 2017), while DOC plays an important role in affecting the transport of metals and organic pollutants,

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influencing photo-chemistry of natural waters and nutrient availability and serving as an important source of microbial substrate (Hope et al., 1997; Battin et al., 2009). Previous studies have recognized the importance of identifying the source and fate of DIC and DOC in surface water transport to elucidate carbon cycling through atmosphere–land–ocean systems (Volk et al., 1997; Maurice and Leff, 2002; Mayorga et al., 2005; Miller, 2011). The species and magnitude of dissolved carbon exchanges within these systems can be determined through the concentration and carbon isotopic composition of DIC ($\delta^{13}C_{DIC}$) and DOC ($\delta^{13}C_{DOC}$) in waters (Telmer and Veizer, 1999; Ye et al., 2015).

Lakes and rivers have traditionally been studied as separate entities for dissolved carbon transport, and a knowledge gap still exists in the dissolved carbon transport in a river-lake continuum. Rivers are considered as either a single channel of flowing water or as a larger system including the river channel floodplain network (Bouwman et al., 2013). Consequently, riverine carbon transport is mostly studied as a continuous system from headwaters to the river mouth without considering in-network lakes within rivers' passageways (Dubois et al., 2010; Iwata et al., 2013). Several studies have noted that rivers and lakes should be considered as a combined conduit and reactor for terrestrial carbon transport across waterscapes (Cole et al., 2007; Tranvik et al., 2009), and the retention process within in-network lakes need to be included for quantifying the biogeochemical filtering of a river-lake continuum (Bouwman et al., 2013). Specifically, existing studies focusing on riverine DIC have reported that partial pressure of carbon dioxide (pCO_2) in rivers and streams can decrease downstream because of CO_2 evasion as water travels away from high CO_2 inputs (Brunet et al., 2009). Some studies have also shown that pCO_2 may also increase downstream if originates in large lakes (Buhl et al., 1991; Flintrop et al., 1996). However, very few studies have looked into how DIC dynamics change in a fluvial

system before and after passing through a lake. For DOC, while extended residence times in lakes could result in lakes functioning as DOC sinks, results to date have been inconsistent indicating that lakes can function as both sources (Kalinin et al., 2016) or sinks (Kang et al., 2016) of DOC. In addition, most studies for dissolved carbon dynamics have been undertaken in Nordic or temperate regions (Pacheco et al., 2014; Chow et al., 2017), but their results may not necessarily reflect the same as a subtropical watershed study.

To assess the influence of an in-network lake on DIC and DOC transport, this study was conducted along the Little River-Catahoula Lake continuum in central Louisiana, USA to discern the dynamics of concentrations and $\delta^{13}C$ isotopic signatures of DIC and DOC across waterscapes. The ultimate goal is to determine the major sources and corresponding biogeochemical processes controlling DIC and DOC dynamics, and to explore whether the subtropical lake function as a carbon sink or carbon source for dissolved carbon transport in the river-lake continuum. The study would test the hypothesis that the DOC pool in the Little River Basin was mainly terrestrially derived, while DIC dynamics were heavily affected by metabolism and CO_2 outgassing, making the in-network lake a sink for dissolved carbon transport.

3.2. METHODS

3.2.1. Little River – Catahoula Lake Continuum

This study was conducted in the lower Little River Basin in subtropical Louisiana, United States, from April 2015 to February 2016 (Figure 3.1). The Little River is formed by the confluence of the Dugdemona River and Castor Creek at a geographical location of 92°21'46" W and 31°47'48" N, the headwaters of which are predominantly forested (DaSilva et al., 2013). The river flows initially southeastwards in north-central Louisiana, and then turns east-

northeastwards into Catahoula Lake (Figure 3.1). Catahoula Lake is the largest natural inland freshwater lake in Louisiana with a surface area of approximately 119 km^2. It is a principal stopover and wintering area for hundreds of thousands of migratory waterfowl and shorebirds. In

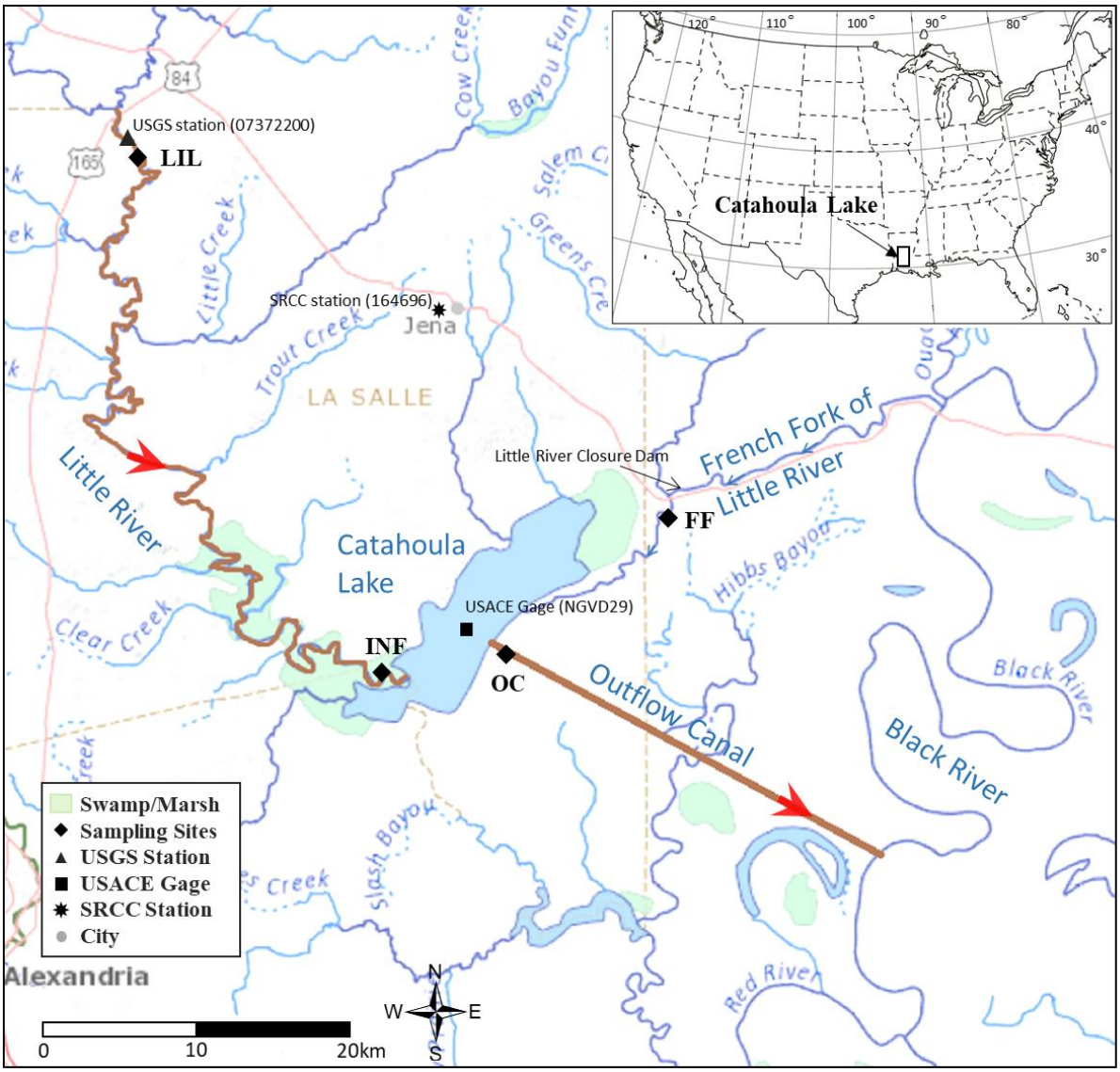

Figure 3.1. Geographical location of the Little River – Catahoula Lake continuum, and its major inflow and outflow (in red lines with arrows for the flow direction) in subtropical Louisiana, the United States. Backwater flow occurred at the French Fork check dam when the Atchafalaya River water stage was high (blue arrows for the flow direction).

1972, a check dam (a.k.a. Little River Closure Dam) and an outflow canal were built at the lake to control water level for creating optimal habitats for migratory birds (Doyle et al., 2002). The

check dam is built across the natural outflow channel at French Fork (Figure 3.1) to prevent outflow from the lake. Previous studies have reported backwater flows to the lake through the dam (Dugué, 2015). Since the French Fork of the Little River is connected to the Black River which flows into the Atchafalaya River, the Catahoula Lake water stage is affected by Atchafalaya River's stage. When the Atchafalaya River stage is lower than 7.3 m, excess water drains to the east to the Black River through the check dam on the French Fork of the Little River. When the Atchafalaya River stage is greater than 7.3 m, the lake receives backwater from Atchafalaya-Red-Mississippi rivers through the Balck River and the check dam on the French Fork (Dugué, 2015; Latuso et al., 2017). The outflow canal is a straight channel of approximately 30 m in width and the outflow is controlled by a sluice gate by the US Army Corp of Engineers. The lake water level is normally maintained high during the winter-spring period and low during the summer–fall period with maximum and average water depth at around 16 and 11 meters, respectively (Dugué, 2015).

Climate in the region can be classified as humid subtropical with long hot summers and short mild winters. The long term annual precipitation is about 1,470 mm (Gaydos et al., 1973). Headwaters of the Little River are mostly covered by pine forests, and the uppermost part of the river above Catahoula Lake flows through a mixed oak-gum bottomland forest interspersed with stands of bald cypress (Gaydos et al., 1973). The variably-inundated lakebed of Catahoula Lake is occupied by herbaceous plants and woody plants at slightly higher elevations on the lake margins including water-elm (*Planera aquatic* J.F. Gmel.), swamp-privet (*Forestiera acuminate* (Michx.) Poir.) and bald cypress (*Taxodium distichum* (L.) Rich.) (Latuso et al., 2017). The surface geology of the river drainage area is dominated by a series of clays, sands, and gravels which unconformably overlie Tertiary deposits (also known as Citronelle and Port Hudson

formations) (Fisk, 1939). The Little River was developed by upon Pleistocene deltaic plains during one or another stage of Pleistocene rejuvenation (Fisk, 1939), and high calcium limestones are distributed in catchments of its headwaters (MWKL, 1972). The dominant soil series in the catchment are the Smithdale and Ruston series. Other important soil series include Ouachita, Jena, Libuse, Gore and Fausse series (NRCS, 2017).

3.2.2. Sampling Design

Four sites were chosen to represent the Little River-Catahoula Lake continuum (Figure 3.1). They include 1) a Little River upstream site (LIL) that was close to the confluence point of the Dugdemona River and Castor Creek where the Little River exits the forested headwater region; 2) a lake inflow site (INF) which was located at Russells Landing, approximately 2,500 m upstream of the western lakeshore wetland; 3) a lake outflow site (OC) which was on the outflow canal about 500 m downstream of the south-central lakeshore; and 4) a backwater site (FF) at French Fork, which was about 900 m west of the check dam (Figure 3.1). This sampling design was to capture dissolved carbon dynamics from the Little River through Catahoula Lake, while the functionality of the lake on carbon transport was explored by the data from the lake inflow (INF) and outflow (OC) sites. French Fork (FF) was selected as an additional site to detect possible effects from backwater.

3.2.3. Field Measurements

From April 2015 to February 2016, monthly field trips were made to conduct in situ measurements on a set of water quality parameters including water temperature, pH, electrical conductivity (EC), and dissolved oxygen (DO) concentration using a YSI 556 multi-probe meter (YSI Inc., Yellow Springs, OH, USA) at about 3 m from the shoreline. During each trip, field measurements were taken at around 9:00AM, 10:00AM, 11:30AM and 1:30PM at the French

Fork (FF), lake outflow (OC), lake inflow (INF) and Little River upstream (LIL), respectively. In addition, chlorophyll *a* fluorescence was also measured with an AquaFluor® handheld fluorometer (Turner Designs, CA, USA) to discern variability in biological activity.

During each field trip water samples were collected at all sites with a grab sampler at 30-50 cm depth below water surface following the water quality parameter measurements. Additional field replicates were taken at the lake outflow (OC) as quality control samples. The samples were analyzed for concentrations of dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and their delta 13 isotope ($\delta^{13}C$). DIC samples collected at each site were stored in 20-ml glass vials with open-top caps and butyl rubber septa. DOC samples were filtered by 0.25 µm nylon syringe filters (Environmental Express, South Carolina, USA) and stored in acid-rinsed high-density polyethylene bottles. Details in DIC and DOC sample preparation and preservation can be found at http://stableisotopefacility.ucdavis.edu/. Water samples (250 ml) collected from April 2015 to January 2016 were also analyzed for silicon (Si), magnesium (Mg) and calcium (Ca), which were acidified with 1:1 HNO_3 to pH < 2 at the time of collection in the field. All samples were stored in a cooler with wet ice during the transportation. After back to the laboratory, element and DIC samples were kept refrigerated and DOC samples were frozen until analyses.

3.2.4. Laboratory Analyses

All water samples were analyzed for DIC and DOC at the University of California Davis, Stable Isotope Facility at a bimonthly interval. DIC samples were analyzed using a GasBench II system interfaced to a Delta V Plus IRMS (Thermo Scientific, Bremen, Germany). DOC samples were analyzed using an O.I. Analytical Model 1030 TOC Analyzer (Xylem Analytics, College Station, TX) interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd.,

Cheshire, UK) utilizing a GD-100 Gas Trap Interface (Graden Instruments). Detailed laboratory procedures can be found at http://stableisotopefacility.ucdavis.edu/.

The isotope composition of DIC and DOC was reported using delta (δ) notation relative to the international standard V-PDB (Vienna PeeDee Belemnite):

$$\delta^{13}C = \left(\frac{R_S}{R_{VPDB}} - 1\right) * 1000‰ \quad (3.1)$$

where R_s is the ^{13}C:^{12}C ratio of a sample, and R_{VPDB} is the ^{13}C:^{12}C ratio of the VPDB sample. The method detection limit and long-term standard deviation for $\delta^{13}C_{DIC}$ as CO_2 were approximately 150 nanomoles and 0.1‰. The analytical precision for $\delta^{13}C_{DOC}$ at DOC concentrations greater than 0.5 ppm was 0.4‰.

All element samples were analyzed with an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Varian Vista MP-X, California, USA) at the W. A. Callegari Environmental Center, Louisiana State University Agricultural Center using EPA Method 200.7. The detection limits for Si, Mg and Ca were 0.36, 0.42 and 0.50 umol L^{-1}, respectively.

3.2.5. Hydrology and Climate Data Collection

Daily river discharge ($m^3 \cdot s^{-1}$) and river stage (m) records of the Little River near Rochelle, Louisiana, which was located about 200 river kilometers upstream of Catahoula Lake, were collected from the United States Geological Survey (USGS) gauge station# 07372200 (Figure 3.1) for the period April 2015 - February 2016. For the same time period daily water depths of Catahoula Lake were obtained from the United States Army Corps of Engineers (USACE) at the gage located in the center of the lake (USACE gage No.: NGVD29, Figure 3.1). Monthly air temperature, precipitation and wind speed records were collected from the national weather station administered by the Southern Regional Climate Center (SRCC) at Jena, Louisiana (SRCC station ID.: 164696, Figure 3.1). For the same period of time, river stage data

of the Atchafalaya River were also obtained from the USGS gauge station at Simmesport, Louisiana (USGS station# 07381490, not shown on Figure 3.1) to determine possible downstream backwater effects on Catahoula Lake.

3.2.6. Data Analysis

The relationship between the frequency and magnitude of daily streamflow of the Little River was expressed as a flow duration curve utilizing the Weibull plotting position formula, which has been adopted as the standard plotting position method by the U.S. Water Resources Council in 1981 (Water Resources Council, 1981). Based on the flow duration curve flow conditions were classified as "High Flows" and "Low Flows", which corresponded to exceedance probabilities less than 10% and greater than 90%, respectively.

Strong positive log-linear relationships of riverine DIC loads with the river discharge were found in this study (Xu, 2013; Gray et al., 2015), which can be described in an equation as below:

$$\ln(DIC_r) = b_0 + b_1 \ln(Q_{day}(t)) + \varepsilon(t) \quad (3.2)$$

$$DIC_l = DIC_r \times BCF \quad (3.3)$$

where Q_{day} represents the daily discharge in liters, DIC_r represents rating curve estimations of daily DIC loads in grams, and $\varepsilon(t)$ is an error term assumed to be normally distributed. b_0 and b_1 are two regression parameters. DIC_l is the loads estimates used in the study, and BCF is the log bias correction factor given by Ferguson (1986) that corrects for the logarithmic transformation consequence of calculating regression parameters using geometric rather than arithmetic mean. The parameter fitting statistics were summarized in Appendix C1 and C2.

To assess the possible difference in carbon dioxide (CO_2) outgassing, we estimated partial pressure of dissolved carbon dioxide (pCO_2) in river and lake waters. We applied the equation developed by Cai and Wang (1998) using measured pH and DIC data:

$$pCO_2 = \frac{[CO_2]}{K_H} = \frac{C_T \{H\}^2}{(\{H\}^2 + \{H\}K_1 + K_1K_2)\, K_H} \quad (3.4)$$

where C_T is the DIC concentration, $\{H\} = 10^{-pH}$, K_H is the solubility constant (Weiss, 1974), and K_1 and K_2 are the dissociation constants of carbonic acid (Harned and Davis, 1943).

The CO_2 flux from surface water to the atmosphere was then calculated using the stagnant-layer model by Cai and Wang (1998):

$$CO_2 \text{ flux} = K_T K_H [pCO_{2(water)} - pCO_{2(air)}] \quad (3.5)$$

where K_T is the gas transfer velocity in cm h^{-1}, $pCO_{2(water)}$ is partial pressure of carbon dioxide in water in µatm, and $pCO_{2(air)}$ is partial pressure of carbon dioxide in air in µatm, which is set as 400 in µatm in this work. K_T was converted from the normalized Schmidt number of 600 (K_{600}) according to the following equation by Jähne and others (1987):

$$k = K_{600} \times \left(\frac{600}{Sc_{CO_2}}\right)^n \quad (3.6)$$

where n is the Schmidt number exponent, which is approximated with 0.5 wind speeds exceeding 3.7 m s^{-1} and increases to 0.75 when wind speeds going below 3.7 m s^{-1} (Guerin et al., 2007). Sc_{CO2} is the CO_2 Schmidt number for a given temperature (Wanninkhof, 1992). K_{600} was calculated based on the equation from Cole and Caraco 1998:

$$K_{600} = 2.07 + 0.215U_{10}^{1.7} \quad (3.7)$$

where U_{10} is the wind speed (in m s^{-1}) normalized to a height of 10 m above the water surface.

Daily loads of DIC in the Little River were computed using the daily discharge data and were summed up to monthly loads. Average lake volume and lake surface area for each month

during the study period were calculated by ArcGIS using water depth data from USACE gauge (No.: NGVD29) and bathymetry data from USGS (Doyle et al., 2002). Monthly retention times of the lake were calculated as the ratio of the monthly lake volume to average daily river discharge of the month. Monthly mass storages of DIC in the Catahoula Lake were calculated as the product of lake volume and lake DIC concentrations assuming equal concentration throughout the water column. When affected by the backwater, lake DIC concentrations was calculated as the average concentrations at lake inflow (INF) and at lake outflow (OC); when not affected by the backwater, lake DIC concentrations was calculated as the average concentrations at lake inflow, at lake outflow and at French Fork (FF). Monthly CO_2 exchanges at the air-water interface were calculated as the product of CO_2 flux and lake surface area of each month.

Differences in mean concentrations and isotopic signatures of DIC, DOC and pCO_2 among sites in the river-lake continuum were tested for statistical significances using the randomization test (Edgington et al., 2007) with the significance level of 0.05. Specifically, statistical comparisons between the Little River upstream and the lake inflow, between the lake inflow and lake outflow and between the Little River upstream and the lake outflow were treated as paired tests. When not affected by the backwater, comparisons between French Fork and other sites were considered as paired tests. In contrast, when affected by the backwater, comparisons between French Fork (FF) and other sites were considered as two sample tests. Any pair with a missing value was removed when paired tests were conducted. The coefficient of variation (CV) was calculated as the ratio of the standard deviation to the mean for average dissolved carbon concentrations for all sites. Linear regressions were used to examine the relationships among different water quality, ambient and hydrological parameters. All statistical analyses were

performed with the SAS Statistical Software package (SAS Institute, Cary, North Carolina) and RStudio.

3.3. RESULTS

3.3.1. Ambient Conditions

During the study period, average monthly air temperature in the area ranged from 6.8 to 28.2 ˚C with the highest in July and the lowest in January (Appendix C3), and water temperature fluctuated similarly in the seasons but with a smaller variation (Table 3.1). Monthly precipitation fluctuated from 13 to 306 mm averaging 119 mm per month, with the lowest in August 2015 and the highest in November 2015 (Appendix C3). Daily discharge of the Little River during the study period fluctuated largely from 0.29 to 484 $m^3 s^{-1}$ with an average of 66 $m^3 s^{-1}$ and a median of 40 $m^3 s^{-1}$, while daily discharge on the sampling dates from April 2015 to February 2016 ranged from 0.3 to 110 $m^3 s^{-1}$ (Figure 3.2). Two "High Flow" events (i.e. discharge > 135 $m^3 s^{-1}$) were observed during the study period (May 19th, 2015 - June 8th, 2015 and January 27th, 2016 – February 4th, 2016), while "Low Flow" periods (i.e. discharge < 0.48 $m^3 s^{-1}$) only occurred in September and October in 2015 (Figure 3.2). Daily lake water depths in the center of the Catahoula Lake varied from 7.3 m to 14.8 m during the study period with an average of 11.1 m, while daily lake depths on the sampling dates during April 2015 - February 2016 fluctuated from 8.2 to 14.8 m (Figure 3.2). In general, the lake was shallower from late August to late October and was deeper during the rest of the year. Accordingly, the lake had a retention time from 96 to 7971 days from April 2015 to February 2016 (Figure 3.3).

The lake water showed a greater seasonal variation in chlorophyll fluorescence with much higher values during August – October 2015 (averaged at 100 AFU), when compared to the three other sites (Table 3.1, Figure 3.3). The river water showed a greater seasonal variation

in electrical conductivity with much higher values from August to October 2015 (averaged at 731 µS cm^{-1}) when compared with waters at other sites. DO concentration and saturation levels were relatively lower at the French Fork than those at other sites, while pH levels at all sites were similar (Table 3.1). Mg and Ca concentrations showed similar seasonal variations among all sites with higher values during August – October 2015, while seasonal Si concentrations fluctuated

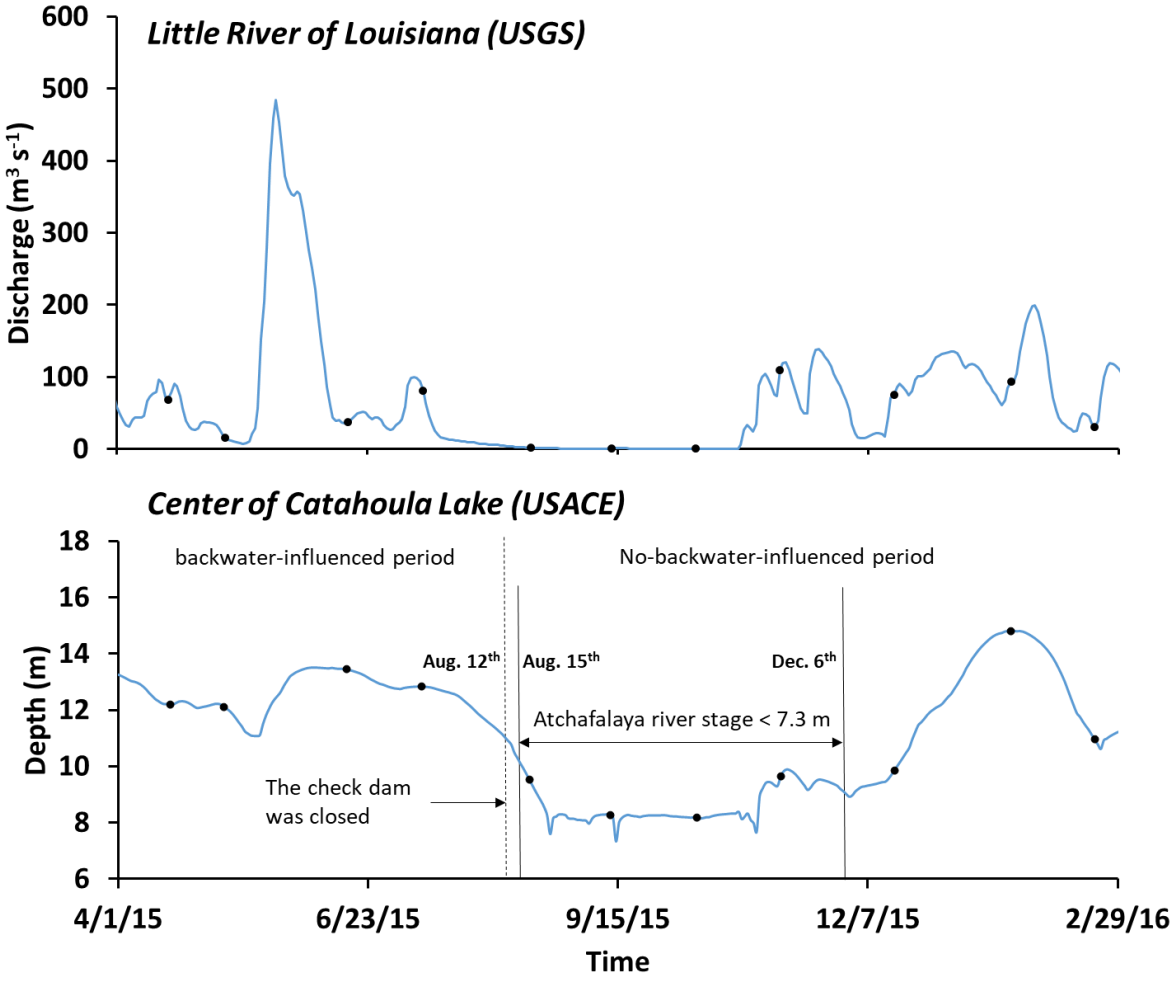

Figure 3.2. Daily discharge of the Little River (above), and daily water depth at the center of Catahoula Lake (below). Black dots represent the sampling dates. The dashed line in the figure below represents the time when the check dam at French Fork was closed (since August 12th, 2015), and the two solid lines indicates the period when the Atchafalaya River stage was less than 7.3 m (August 15th, 2015 to December 6th, 2015).

differently at all sites. All significant Pearson correlation coefficients (Pearson's *r*) between tested variables in the studied river-lake continuum were listed in Table 3.2.

Table 3.1 Basic statistics of water quality parameters including fluorescence, water temperature (water temp), electrical conductivity (EC), dissolved oxygen saturation (DO %), dissolved oxygen concentration (DO conc.), partial pressure of carbon dioxide (pCO_2), pH, silicon concentration (Si conc.), magnesium concentration (Mg conc.), and calcium concentration (Ca conc.) measured at the Little River upstream (LIL), Little River inflow (INF), Catahoula Lake Outflow Canal (OC), and Catahoula Lake check dam at French Fork (FF) during the study period. All data are presented as "Mean ± *Standard deviation* (Minimum – Maximum).

	LIL (n = 11)	INF (n = 11)	OC (n = 11)	FF (n = 10)
Fluorescence (AFU)	48 ± *12* (27-74)	39 ± *11* (27-59)	55 ± *33* (18-123)	51 ± *22* (26-93)
Water temp. (˚C)	21 ± *7* (8-31)	23 ± *7* (11-31)	21 ± *6* (9-30)	22 ± *7* (9-31)
EC (µS cm^{-1})	283 ± *307* (76-962)	113 ± *49* (64-221)	81 ± *42* (22-177)	88 ± *38* (50-177)
DO % (%)	66 ± *14* (46-85)	61 ± *17* (39-100)	67 ± *17* (46-96)	49 ± *15* (24-69)
DO conc. (mg L^{-1})	5.9 ± *1.9* (3.6-8.7)	5.3 ± *1.6* (2.9-8.2)	6.1 ± *1.9* (3.6-9.7)	4.5 ± *1.8* (1.8-7.4)
pCO_2 (µatm)	8212 ± *4774* (1987-19142)	6545 ± *3502* (1535-12345)	5675 ± *4864* (459-13338)	6493 ± *4374* (1184-14042)
pH	6.4 ± 0.*6* (5.6-7.2)	6.4 ± 0.*5* (5.8-7.2)	6.4 ± 0.*7* (5.6-7.3)	6.6 ± 0.*5* (5.9-7.2)
Si conc. (µmol L^{-1})	204 ± *83* (57-319)	190 ± *93* (26-384)	253 ± *175* (75-678)	222 ± *172* (93-602)
Mg conc. (µmol L^{-1})	89 ± *41* (45-177)	61 ± *13* (40-80)	78 ± *27* (45-137)	99 ± *33* (53-162)
Ca conc. (µmol L^{-1})	213 ± *106* (117-471)	135 ± *31* (88-189)	142 ± *48* (92-246)	168 ± *67* (84-327)

3.3.2. River-lake Continuum of DIC, DOC and $\delta^{13}C$

A decreasing trend in dissolved inorganic carbon concentrations was found from the river upstream (LIL) to the lake inflow (INF), and then to the lake outflow (OC) during the study period (Table 3.3). Specifically, significant decreases in DIC concentrations were observed from the river upstream to the lake outflow and from the lake inflow to the lake outflow (Table 3.4). Average DOC concentration had a decreasing trend as well from the river upstream to the lake outflow (Table 3.3), and significant decreases also

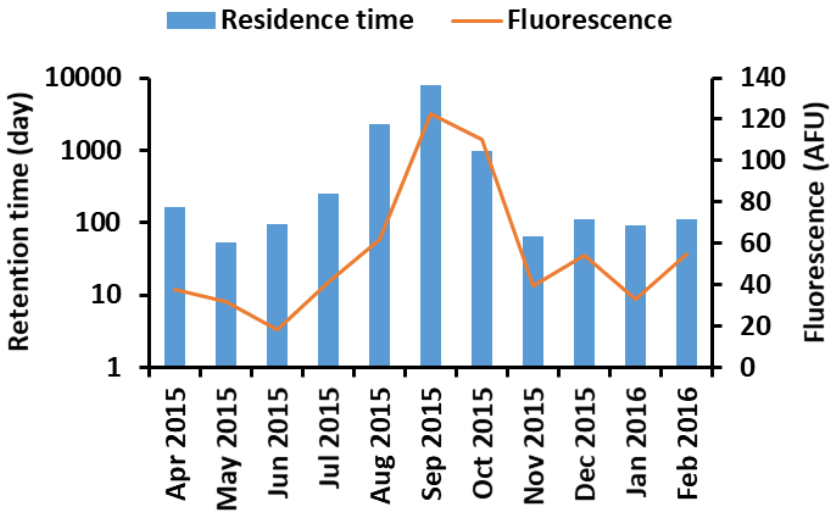

Figure 3.3. Monthly lake retention time and lake fluorescence levels from April 2015 to February 2016.

existed from the river upstream to the lake inflow, from the lake inflow to the lake outflow and from the river upstream to the lake outflow (Table 3.4). Average DIC concentration at the French Fork (FF) was higher than those at both lake inflow and outflow, while average DOC concentration at the French Fork was in between (Table 3.3). No significant difference was found in $\delta^{13}C$ among all sites (Table 3.4).

Table 3.2. Significant Pearson correlation coefficients (r) between tested variables at all sites.

	Pearson's *r*			
Variables	LIL (n = 11)	INF (n = 11)	OC (n = 11)	FF (n = 10)
EC and DIC	0.96^{***}	0.57^{*}		0.85^{**}
EC and $\delta^{13}C_{DIC}$	0.88^{***}	0.57^{*}		0.85^{***}
$\delta^{13}C_{DIC}$ and fluorescence			0.73^{*}	
$\delta^{13}C_{DIC}$ and DOC	-0.79^{**}			
$\delta^{13}C_{DIC}$ and 1/(Ca+Mg)#	-0.81^{**}	-0.88^{***}	-0.64^{*}	-0.78^{*}
$\delta^{13}C_{DOC}$ and Temp.	-0.75^{**}	-0.77^{**}		-0.85^{**}
DOC and Discharge	0.70^{*}			
DOC and Lake Ret. Time##			0.95^{***}	

* Significance levels: $p < 0.05$.
** Significance levels: $p < 0.01$.
*** Significance levels: $p < 0.001$.
# From April 2015 - January 2016, n=11 for LIL/INF/OC and 10 for FF.
From August 2015 - November 2015, n=4 for OC.

The check dam was closed on August 12th, 2015. At the same time, the river stage of the Atchafalaya River was lower than 7.3 m from August 15th, 2015 to December 6th, 2015 (Figure 3.2). This information indicated that the Catahoula Lake received its major inflow from the Little River and backwater through the French Fork of Little River until August 12th, 2015, but only received the major input from the Little River afterwards during the study period. As a result, it is also necessary to present the river-lake continuum of DIC, DOC and $\delta^{13}C$ separately for the backwater-influenced period and no-backwater-influenced period. Since field

Table 3.3. Average concentrations and stable isotope values of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) observed at all sites for the entire study period (April 2015 - February 2016), as well as for the backwater-influenced period (April 2015 - July 2015) and the no-backwater-influenced period (August 2015 - February 2016). Data are presented as mean ± *standard deviation*.

Time	Location	Site	n	DIC		DOC	
				Conc. (μmol L^{-1})	$\delta^{13}C$ (‰)	Conc. (μmol L^{-1})	$\delta^{13}C$ (‰)
Apr 2015 - Feb 2016	Upstream	LIL	11	848 ± *661*	-18.5 ± *4.1*	1213 ± *309*	-29.3 ± *0.9*
	Inflow	INF	11	482 ± *107*	-18.0 ± *4.4*	1103 ± *246*	-29.2 ± *0.9*
	French Fork	FF	10	529 ± *133*	-19.4 ± *4.1*	1034 ± *223*	-29.3 ± *1.0*
	Outflow	OC	11	399 ± *149*	-17.9 ± *3.3*	969 ± *211*	-29.0 ± *1.1*
Apr 2015 - Jul 2015	Upstream	LIL	4	563 ± *230*	-20.1 ± *2.6*	1283 ± *235*	-29.5 ± *0.4*
	Inflow	INF	4	501 ± *44*	-17.3 ± *1.5*	1245 ± *144*	-29.4 ± *0.4*
	Backwater	FF	4	561 ± *88*	-19.7 ± *1.7*	1031 ± *235*	-29.6 ± *0.1*
	Outflow	OC	4	492 ± *75*	-19.7 ± *1.5*	1063 ± *127*	-29.5 ± *0.3*
Aug 2015 - Feb 2016	Upstream	LIL	7	1011 ± *785*	-17.6 ± *4.7*	1172 ± *356*	-29.2 ± *1.2*
	Inflow	INF	7	471 ± *134*	-18.4 ± *5.5*	1022 ± *264*	-29.1 ± *1.1*
	Lake	FF	6	507 ± *162*	-19.3 ± *5.4*	1035 ± *237*	-29.1 ± *1.3*
	Outflow	OC	7	346 ± *158*	-16.8 ± *3.7*	915 ± *239*	-28.8 ± *1.4*

measurements and sample collections for August 2015 were conducted several days after the time when the check dam was closed, August 2015 was not considered as one of the months strongly affected by the backwater. Therefore, we consider April 2015 – July 2015 as the backwater-influenced period and August 2015 – February 2016 as no-backwater-influenced period. During the backwater-influenced period, French Fork (FF) was the site representing backwater input to the Catahoula Lake, while during the no-backwater-influenced period French Fork represented an extension of the lake body.

Table 3.4. P-values by randomization tests for comparisons between any two sites in concentrations and stable isotope values of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) for the entire study period (April 2015 - February 2016), as well as for the backwater-influenced period (April 2015 - July 2015) and the no-backwater-influenced period (August 2015 - February 2016).

		Apr 2015 - Feb 2016			Apr 2015 - Jul 2015			Aug 2015 - Feb 2016		
		n	P-value		n	P-value		n	P-value	
			Conc.	$\delta^{13}C$		Conc.	$\delta^{13}C$		Conc.	$\delta^{13}C$
DIC	LIL and INF	22	0.084	0.57	8	0.74	<0.0001	14	0.087	0.29
	INF and OC	22	0.038	0.9	8	0.88	<0.0001	14	0.021	0.25
	LIL and OC	22	0.0096	0.5	8	0.48	0.77	14	<0.0001	0.56
	FF and LIL	21	0.17	0.62	8	0.94	0.75	13	0.25	0.60
	FF and INF	21	0.36	0.48	8	0.28	0.084	13	0.21	0.91
	FF and OC	21	0.0016	0.22	8	<0.0001	0.77	13	0.063	0.19
DOC	LIL and INF	22	0.038	0.43	8	0.51	0.37	14	<0.0001	0.82
	INF and OC	22	0.044	0.18	8	<0.0001	0.12	14	0.28	0.094
	LIL and OC	22	0.014	0.11	8	<0.0001	0.75	14	0.099	0.078
	FF and LIL	21	0.14	0.98	8	0.24	0.75	13	0.22	0.31
	FF and INF	21	0.51	0.87	8	0.2	0.41	13	0.56	0.63
	FF and OC	21	0.79	0.33	8	0.6244	0.50	13	0.59	0.43

In the backwater-influenced period, DIC concentration did not show a significant difference after passing through the lake, while riverine DOC declined significantly (Table 3.4). The backwater showed significant higher DIC concentrations but a similar DOC level compared to the DIC and DOC concentrations at the lake outflow (Table 3.3 and 3.4). Average $\delta^{13}C_{DIC}$ at the lake inflow was found significantly higher than that at the river upstream and lake outflow, while no significant difference was detected in $\delta^{13}C_{DOC}$ among sites (Table 3.3 and 3.4).

For the no-backwater-influenced period, average DIC concentration went down from the river upstream to the lake inflow, and decreased significantly from lake inflow to the lake outflow and from the river upstream to lake outflow (Table 3.3 and 3.4). Average DOC concentration decreased significantly from the river upstream to the lake inflow and did not change significantly after passing through the lake (Table 3.3 and 3.4). However, it is worth noting that throughout the study period only in September and October DOC concentrations increased after passing through the lake (from 890 to 1218 umol L^{-1} and from 520 to 558 umol L^{-1}, respectively). Excluding these two months, a significant decrease in DOC concentrations was observed from lake inflow (averaged at 1150 umol L^{-1}) to lake outflow (averaged at 926 umol L^{-1}, $p < 0.0001$, n = 10) in the no-backwater-influenced period. No significant difference was found among all sites for $\delta^{13}C$ (Table 3.3 and 3.4).

3.3.3. Seasonal Variations in DIC, DOC and $\delta^{13}C$ Along The River-lake Continuum

From April 2015 to February 2016, DIC concentrations ranged from 349 to 2063, from 208 to 573, from 142 to 588 and from 344 to 715 umol L^{-1} for the river upstream (LIL), lake inflow (INF), lake outflow (OC) and French Fork (FF) locations, respectively (Figure 3.4). Specifically, DIC concentrations in the river upstream showed a greater seasonal variation, which increased drastically during August 2015 – October 2015 and dropped substantially in

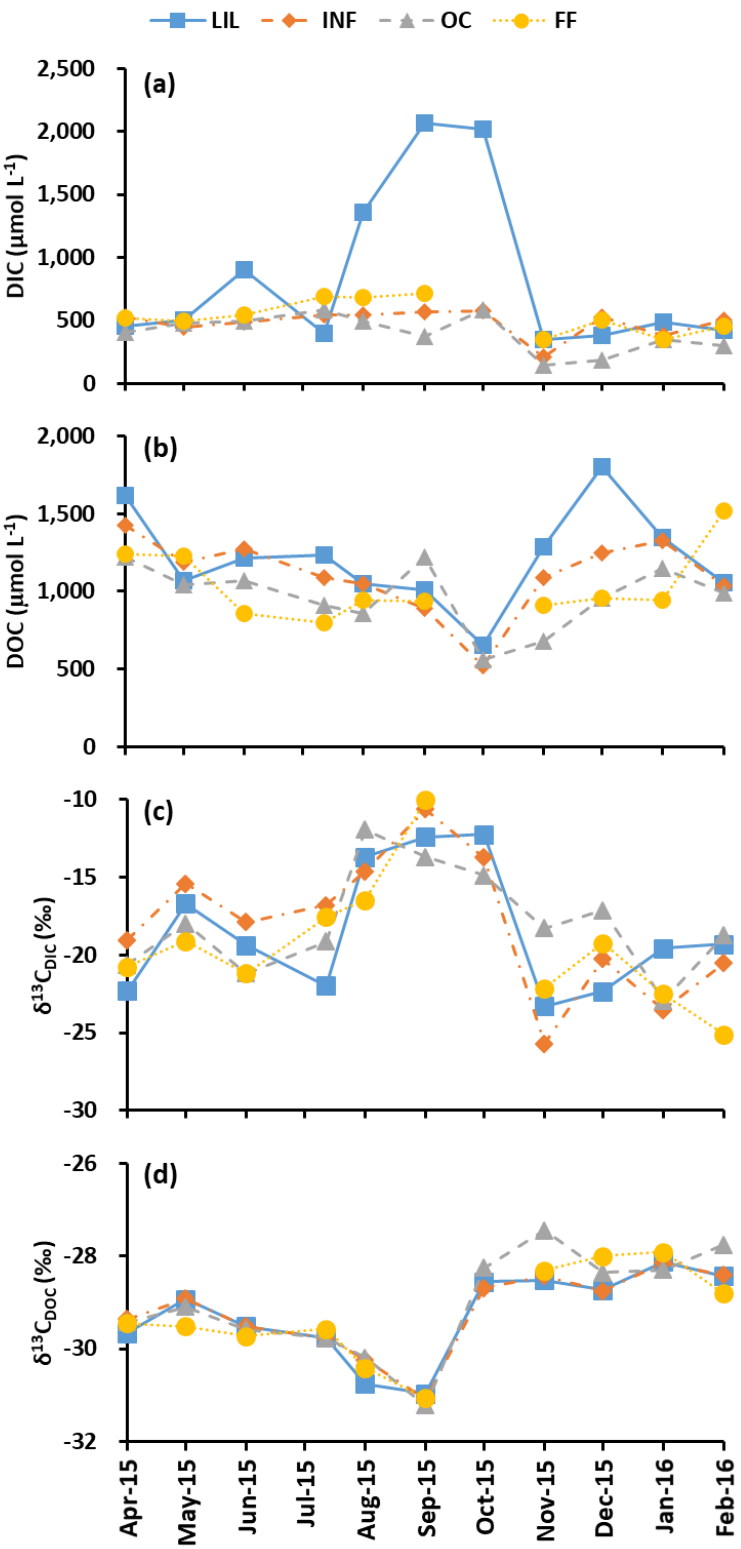

Figure 3.4. Monthly observations of a) DIC concentrations, b) DOC concentrations, c) $\delta^{13}C_{DIC}$ and d) $\delta^{13}C_{DOC}$ 2016 for all sites from April 2015 to February 2016.

November 2015. The CV of DIC concentrations were 77.9, 22.3, 37.3 and 25.2 for the river upstream, lake inflow, lake outflow and French Fork, respectively. DOC concentrations ranged from 654 to 1799, from 520 to 1428, from 558 to 1223 and from 801 to 1517 umol L^{-1} for the river upstream, lake inflow, lake outflow and French Fork, respectively (Figure 3.4). Seasonal DOC concentrations at all sites tended to decrease continuously from April 2015 to October 2015 and then increased sharply. Different from DIC, seasonal variations of DOC concentrations seemed to be similar in the river-lake continuum, and the CV of DOC concentrations were 25.5, 22.3, 21.8 and 21.5 for the river upstream, lake inflow, lake outflow and French Fork, respectively.

Carbon-13 isotope of DIC fluctuated largely at all sampling sites, specifically, from -23.3 to -12.3 ‰ at the river upstream, from -25.7 to -10.6 ‰ at the lake inflow, from -22.9 to -11.9 ‰ at lake outflow, and from -25.1 to -10.0 ‰ at French Fork. The seasonal trend of $\delta^{13}C_{DIC}$ showed a similar trend at these sites, with higher values in August 2015, September 2015 and October 2015 (Figure 3.4). When compared $\delta^{13}C_{DIC,}$ $\delta^{13}C_{DOC}$ showed much smaller variation, i.e., from -31.0 to -28.1 ‰ at the river upstream, from -31.1 to -28.1 ‰ at the lake inflow, from -31.2 to -27.4 ‰ at the lake outflow, and from -31.1 to -27.9 ‰ at French Fork. Seasonal variations of $\delta^{13}C_{DOC}$ for all sites were similar as well, generally decreasing from April 2015 to September 2015 and increasing dramatically in October 2015 and were then relatively stable until the end of the study period (Figure 3.4).

3.3.4. Dissolved Inorganic Carbon Budgeting

All sites of this river-lake continuum showed higher partial pressure of CO_2 (over 9000 µatm) from April to July. Afterwards, pCO_2 kept decreasing through December and then increasing at all sites (Figure 3.5). Across the river-lake continuum, pCO_2 showed a significantly

decreasing trend from the river to the lake inflow ($p < 0.001$, n = 10) and from the lake inflow to lake outflow ($p < 0.001$, n = 10) during July – December. Monthly CO_2 outgassing from the lake was observed throughout the study period ranging from 2860 to 42071 t month^{-1} with an average of 19821 t and a median of 14928 t month^{-1} (Figure 3.5).

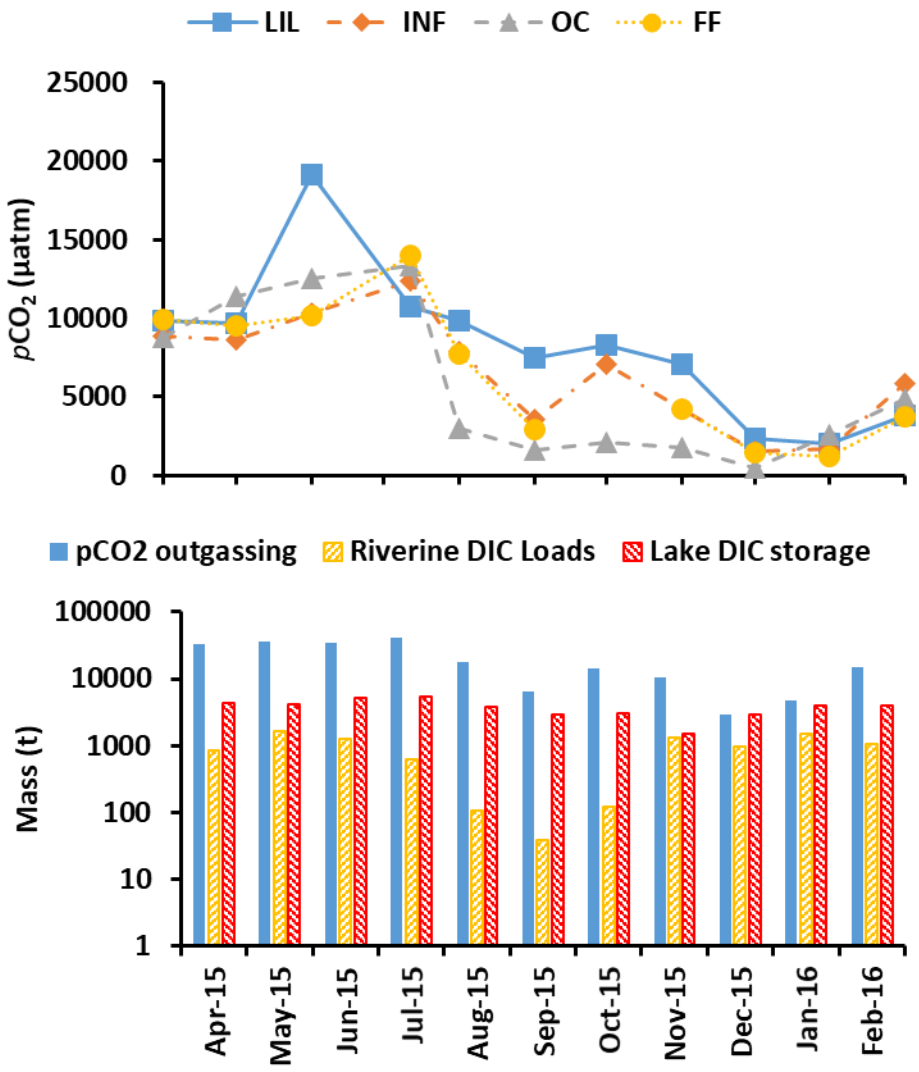

Figure 3.5. Monthly partial pressure of carbon dioxide (pCO_2) at all sites (above), and monthly DIC loads from the Little River, DIC lake storage and CO2 outgassing at Catahoula Lake (below).

b_0 and b_1 in equation (1) are 1.68 and 0.69, respectively (Appendix C1). The mean squared error, R^2 and adjusted R^2 of the rating curve are 0.0673, 0.971 and 0.968, respectively

(Appendix C2). More information for the statistical performance of equation (1) including 95% confidence limits and 95% prediction limits can be found in Appendix C2. Monthly loads of DIC in the Little River showed a seasonal trend closely correlated to the river discharge, with the maximum in May and the minimum in September ranging from 36 to 1584 t with an average of 825 t $month^{-1}$ (Figure 3.5). DIC mass storage in the lake maximized in July (5838 t) and minimized in November (1485 t) averaging at 3819 t $month^{-1}$ (Figure 3.5).

3.4. DISCUSSIONS

3.4.1. Terrestrial and Autochthonous Sources for Dissolved Organic Carbon

Headwaters of the Little River are mostly forested, suggesting that plant residues should be dominated by C_3 vegetation. Previous studies (e.g. O'Leary, 1988) have shown that the $\delta^{13}C$ of organic matter is primarily dependent on the photosynthetic pathway of the plant from which it is derived (-27 to -30 ‰ for C_3 plants and -12 to -14‰ for C_4 plants). The isotopic signature of dissolved organic carbon found in this study was about -29‰, hence, reflecting a dominating pool of terrestrial carbon in the river water. Soils have been reported as the main sources of riverine DOC in similar cases, the transport of which is always considered as a two-stage process: DOC is produced in soils and then transported to drainage networks (Evans et al., 2002; Evans et al., 2007). In this succession, the DOC production rate is positively influenced by environmental conditions such as temperature and wet-dry cycles that promote microbial activity and fungal abundance (Kalbitz et al., 2000), which may explain the negative correlation between temperature and riverine $\delta^{13}C_{DOC}$ and the positive relationship between river discharge and DOC concentrations at the river site (Table 3.2). A recent study reported similar findings; Kalinin et al. (2016) observed strong hydrologic controls on DOC concentrations and export patterns in the Bull Trout Watershed in central Idaho, whereby DOC concentration in the inflow stream

increased with discharge across the range of flows, and there did not appear to be a dilution effect or source depletion.

In the subtropical Little River – Catahoula Lake continuum, autochthonous DOC derived from aquatic phytoplankton cannot be neglected during the productive period. Catahoula Lake was much more productive during August – October 2015 due to the warm temperature, long water residence time and an abundance of phytoplankton (Figure 3.3), as reflected by the high in situ fluorescence measurements. During this period, autochthonous processes could become increasingly important and shift major DOC sources to autochthonous carbon. It is worth noting that DOC concentrations were strongly positively correlated with the lake retention time in the Catahoula Lake during August - November 2015 (Table 3.2), which is different from the notion found in other climate regions that DOC that is retained within the lake for longer periods of time should experience greater biological processing resulting in lower concentrations (Schindler et al., 1997; Weyhenmeyer et al., 2012). Previous studies on North Temperate Lakes have estimated that lakes with residence times less than 1 year exported approximately 60% of the DOC, whereas lakes with residence times greater than 6 years mineralized approximately 60% of the DOC (Hanson et al., 2011). It is known that photosynthesis preferentially utilizes the ^{12}C form of carbon (Keough et al., 1998). Therefore, photosynthesis in the studied lake may have played a more influential role over respiration driving dissolved organic carbon dynamics, especially when the lake becomes more productive as shown by a positive correlation between $\delta^{13}C_{DIC}$ and fluorescence at the lake outflow (Table 3.2).

3.4.2. Shifting Lake Dissolved Organic Carbon Sink-and-source Dynamics

Catahoula Lake plays a shifting role of sink-source dynamics for dissolved organic carbon mainly due to the changes in lake productivity. Studies found that respiration dominates

over primary production in lakes sustained by allochthonous organic inputs (Del Giorgio and Peters, 1993; Jansson et al., 2000). The allochthonous carbon input from rivers can be stored and mineralized in the lakes through sedimentation and in-lake mineralization (Hanson et al., 2011). However, lakes with high autochthonous carbon production could be also a source for DOC. From August to October, the longer residence time of the lake could allow phytoplankton more time to utilize nutrients, thus significantly promoting algae growth and improving autochthonous DOC production. Previous studies have revealed that water residence time is more likely to be important for algae bloom than nutrient concentration. For instance, Lee et al. (2011) has reported that residence time had a much stronger relationship to chlorophyll *a* concentration than chemical factors such as diverse nutrient concentrations in the Sueo dam reservoir at Korea, and it best explained the relation of water status to algae growth (Lee et al., 2011). Maberly et al. (2002) also studied small upland lakes in the English Lake District and demonstrated that short residence time supplied an unsuitable environment for the growth of nitrogen-fixing cyanobacteria. Increased autochthonous carbon production may also explain the dramatic increase of $\delta^{13}C_{DOC}$ in October at the studied lake. In addition, Catalan et al. (2016) analyzed a compilation of 305 existing field and laboratory measurements and found a negative relationship between the rate of organic carbon decay and water retention time, showing that organic carbon reactivity decreases as water retention time increases. This may also contribute to the DOC source behavior of the lake for the studied case.

Similar conditions have been observed in other climate regions as well. For instance, Goodman et al. (2011) reported that a shift in the role of subalpine lakes in Idaho, USA from a DOC sink to a source throughout the summer due to an increase in-lake DOC production when evaluated by differences in DOC concentration between lake inflows and outflows (Goodman et

al., 2011). Since higher temperatures favor aquatic bioactivity, the shift of the role for DOC transport through lakes could be more prevalent in subtropical and tropical environments. Future studies are needed to assess the process of lakes in other climates, and also by including an analysis of particulate inorganic and organic carbon.

3.4.3. Influential Sources for Dissolved Inorganic Carbon

Most dissolved inorganic carbon in the Little River-Catahoula Lake continuum originates from ^{13}C depleted sources such as in situ organic matter, as suggested by the low $\delta^{13}C_{DIC}$ values compared with many existing studies (Brunet et al., 2005; Dubois et al., 2010; Karim et al., 2011; Shin et al., 2015). Due to the input of terrestrial C_3 plant residues to the water and the fact that DOC accounts for the majority of net respiration as well as most of the respired non-sinking organic carbon, the $\delta^{13}C$ of derived CO_2 from these sources should be around -29 to -27‰ (Santana-Falcon et al., 2017). With a 7–11‰ isotopic fractionation when CO_2 is dissolved and converted to DIC (Cerling et al., 1991; Zhang et al., 1995), $\delta^{13}C_{DIC}$ values in this study are expected to range from -22‰ to -16‰, which is similar to the field observations. The negative correlation between $\delta^{13}C_{DIC}$ and DOC in the river upstream also suggests a significant effect of aquatic respiration in riverine DIC dynamics (Table 3.2), which has been shown previously in other cases at temperate regions (Lennon et al., 2006; Kluijver et al., 2014). Similar with this, Dubois et al. (2010) reported that the $\delta^{13}C_{DIC}$ in the lower Mississippi watershed (ranged from −11.5‰ to −7.0‰) is considerably depleted when compared to the theoretical $\delta^{13}C_{DIC}$ value estimated from a 1:1 mixture of soil and carbonated-derived DIC. The authors attributed the depleted values to respiration of organic matter which added ^{13}C depleted carbon to the inorganic carbon pool in the lower Mississippi (Dubois et al., 2010).

Soil respired CO_2 could also be influential as one of the ^{13}C depleted sources, especially during the period with heavy rainfall. Intense precipitation could wash out highly ^{13}C-depleted soil CO_2 accumulated in the pore spaces from the catchment areas and cause an overall drop in in-stream ^{13}C values, which could be a reason why all sites had sharp drops in $\delta^{13}C_{DIC}$ in November 2015. This effect could be more obvious in subtropics/tropics since soil CO_2 levels in these areas are generally higher than those in temperate, alpine, and arctic regions (Brook et al., 1983).

In addition, DIC dynamics in the studied river-lake continuum can be also affected by carbonate weathering, which releases Ca and/or Mg (Marx et al., 2017). The close relation we found between $\delta^{13}C_{DIC}$ and concentrations of Ca and Mg at all sites suggests that the increase in $\delta^{13}C_{DIC}$ values may have been caused by the same process that increased Ca and Mg concentration. Previous studies have reported that weathering processes, as one of the main drivers of carbon fluxes in arctic, subarctic and circumboreal waters, is particularly influential during low flow conditions (Jantze et al., 2015; Tank et al., 2012). In this study, the seasonal highs of $\delta^{13}C_{DIC}$ and Ca/Mg concentrations at all sites during the low flow period (August 2015 to October 2015) may have been resulted from an increased proportion of DIC from the sources with high $\delta^{13}C_{DIC}$ such as soil carbonate weathering.

3.4.4. Lake as A Sink for The Down-network Dissolved Inorganic Carbon Transport

Except the months with continuous low river discharges (August to October, Figure 3.2), Little River carried a considerable amount of dissolved inorganic carbon to the Catahoula Lake compared to the lake storage. The observed dissolved inorganic carbon concentrations in the Little River are consistent with other publications taken in the similar climate regions (e.g. Huang et al., 2012). There were studies reporting the hysteresis effect in carbon concentrations

with changing discharge. However, since those were mainly for DOC (e.g. Butturini et al., 2016) and there was no sufficient data to model the hysteretic loops of DIC, the hysteresis effect was neglected in the DIC load estimates.

The effect of CO_2 degassing may overwhelm other DIC inputs in the Catahoula Lake, making it a sink for down-network DIC transport. Relatively less CO_2 outgassing in September, December and January was found in this study, which could be attributed to the greater carbon fixation over consumption in the productive period (September) and the decreased carbon consumption as a result of low water temperature depressing respiration (December and January). It is a sign that metabolism could create substantial variation in DIC/ $\delta^{13}C_{DIC}$ (Tranvik et al., 2009). However, if the balance between respiration and production of organic matter primarily controlled pCO_2 and $\delta^{13}C_{DIC}$, a tight correlation would be expected between $\delta^{13}C_{DIC}$ and pCO_2 (Kluijver et al., 2014), which was not observed in this study. In contrast, the strong magnitude of CO_2 outgassing from the lake indicates the significant influence of air-lake CO_2 exchange on the lake DIC budget. In some previous studies, CO_2 outgassing has been recognized as the largest DIC export from the lake, which could be greater than riverine outflow and the CO_2 consumption by the aquatic photosynthesis (Weiler, 1974; Weiler, 1975; Finlay et al., 2010). For example, Weiler (1974, 1975) estimated high gas evasion fluxes from lakes Erie and Ontario (mesotrophic-eutrophic lakes), which were double to triple the basin-wide estimates of primary production. Similar with our study, Finlay et al. (2010) reported two Canadian lakes (i.e., Lake Diefenbaker and Buffalo Pound within the Qu'Appelle River catchment) functioning as a sink for DIC owing to CO_2 efflux. Additionally, for CO_2 efflux from lakes, a greater emission of CO_2 from subtropical/tropical lakes has been reported compared to their temperate

counterparts (Tranvik et al., 2009). Furthermore, in this study the backwater contained significantly higher DIC concentrations, which could offset the sink function of lake.

3.5. CONCLUSIONS

This study investigated the connectivity of dissolved carbon in a subtropical river-lake continuum over a year in the southern United States. The findings from the study show that the in-network lake sink-source dynamics vary for dissolved organic carbon while acting as a sink for the down-network dissolved inorganic carbon transport. The DOC pool in the studied watershed is dominantly terrestrially derived, controlled by the runoff-induced hydrological connectivity. In the receiving lake waterbody, however, autochthonous DOC production derived from aquatic phytoplankton cannot be neglected during the warm productive period. As a result, whether the lake functions as a sink or a source for DOC is mainly affected by the lake productivity, which is in turn controlled by the water residence time. In contrast, DIC in the studied river-lake continuum is mainly from ^{13}C depleted sources like in situ organic matter biodegradation and soil respiration derived CO_2. Weathering of carbonic rocks could also play a role affecting variations of DIC and $\delta\,^{13}C_{DIC}$. Different from DOC, the combined effect of metabolism and CO_2 outgassing controlled the DIC dynamics in the in-network lake. However, this functionality of the lake could be offset by the backflow containing high DIC. The role of the in-network lake for the down-network dissolved carbon transport could be enhanced in the subtropical/tropical regions compared to other climate regions since higher temperatures favor aquatic bioactivity. Although this study was conducted in a subtropical humid region, the findings may have implications for carbon transport across waterscapes in other climates. Given the abundance of lakes in fluvial networks, integrating sink-source behavior of in-network lakes

in the fluvial dissolved carbon transport could be an important step toward improved interpreting and modeling of network-scale or regional-scale carbon dynamics in these systems.

CHAPTER 4. METAL TRANSPORT IN A LOW-GRADIENT RIVER-LAKE CONTINUUM IN SUBTROPICAL LOUISIANA, USA

4.1. INTRODUCTION

The multiple interacting spatial scales and dimensions of the biogeochemical connectivity between rivers and lakes can have a strong influence on watershed and fluvial network element dynamics (Covino, 2017). Rivers are the main linkage transferring elements from land to ocean, which carry dissolved and suspended materials and function primarily as a facilitator (Vorosmarty et al., 2000; Walling and Fang, 2003). Interspersed within river networks, lakes can substantially affect the timing, form, and magnitude of down-network element export through nitrogen retention, carbon burial and carbon dioxide emission (Cole et al., 2007; Covino, 2017; Harrison et al., 2009; Xu and Xu, 2018a). Previous inventories have recognized lakes as biogeochemical hot spots within fluvial networks (McClainet al., 2003). Due to the significance of lakes in the areal extent of continental waters (Downing, 2006; Downing, 2010) and its corresponding influence at watershed, regional, continental and global scales (Bouwman et al., 2013; Covino, 2017; Jones, 2010; Powers et al., 2014; Tranvik et al., 2009), it remains a research frontier to study lakes in the context of a connected fluvial network.

The transport of major and trace metals in a river-lake network could have a great environmental and ecological impact to aquatic systems. The weathering of minerals has been traditionally considered as the most important factor in element transports in rivers and lakes (Martin and Meybeck, 1979; Roy et al., 1999), while biologic and anthropogenic activities have also been claimed to play an increasing role to the water chemistry in the recent decades (Drever, 1994; Lopez1 et al., 2006; Kang et al., 2019). Certain metals (e.g., Ca, Mg, Fe) have been reported to be fundamental in supporting structural development of organisms and primary production (Ludwig et al., 2009; Meybeck, 1982; McLaughlin and Wimmer, 1999; Rabalais,

2002), while some heavy metals have been recognized to produce considerable harm to environment and human health (Naimo, 1995; Jezierska et al., 2009). The characterization of spatial and temporal variability of metal cycling in rivers and lakes is crucial to identify sources and sinks of metals as well as their transport modes and to understand the coordination of biological, geological and chemical factors in these processes.

However, our knowledge is limited about the metal chemistry of water across a river-lake continuum. On one hand, in previous inventories lakes and rivers have mostly been separately investigated for metal dynamics. Rivers are mostly considered as the main channel plus river floodplains, and riverine metal transport is often investigated as a conduit from headwater to river mouth ignoring lakes in its network (Bouwman et al., 2013). On the other hand, existing studies of metal dynamics considering the biogeochemical connectivity between lakes and rivers were mostly looking at sediment metals (Ilina et al., 2016; Thorslund et al., 2017), the results of which may not be applicable for a metal chemistry study of water. Only a few studies were conducted recently reporting the metal distribution in water in the river-lake system. For instance, in a study tracking heavy metal contamination in the waters and sediments of an urban zone-river-oxbow lake system at the border between Germany and Poland, Ciazela et al. (2018) reported that the scale of metal contamination in oxbow lakes with different stages of evolution was largely modified by the extent of permanent connection with the river and the frequency of temporal connection with the river during flooding. To our knowledge, up to now no study has been conducted for metal transports in water from the upstream of an inflow river to the outflow of a lake within the connected fluvial network.

Motivated by that, this study was conducted to assess the spatial and seasonal dynamics of major and trace metal concentrations and their atomic ratios along a river-lake continuum at a

low-gradient subtropical watershed in Louisiana, USA. Three scientific questions are addressed in this study: 1) how do metal concentrations in the river differ from those in the downstream receiving lake; 2) what are the main biogeochemical processes controlling the metal dynamics in the river and the lake, and 3) whether the lake and river act as a source or a sink for metal dynamics in a river-lake continuum? This study would test the hypothesis that the Little River functioned as a sink for metal transport mainly due to sedimentation and biological immobilization, while Catahoula Lake acted as a metal source due to a greater weathering intensity in the lake.

4.2. METHODS

4.2.1. Site Description

This studied low-gradient river-lake continuum is located in central Louisiana, Southern United States. The river, Little River, is a 4^{th}-order river draining approximately 5000 km^2 before flowing into a relatively shallow lake, Catahoula Lake (Figure 4.1). Its headwaters are predominately covered by intensively managed pine forests (Xu and Xu, 2018b). During 1990-2008, the average annual concentrations (±standard deviation) of total suspended solid (TSS) and total phosphorus (TP) from the headwaters of the river have been reported to be 25 (±7) and 0.11 (±0.03) $mg \cdot L^{-1}$, respectively (Xu and Xu, 2018b). Starting from the confluence point of the Dugdemona River and Castor Creek (92°21'46" W and 31°47'48" N), the river flows through a mixed oak-gum bottomland forest interspersed with stands of bald cypress and enters the Catahoula Lake at 92°9'47" W and 31°28'7 N.

As the largest natural inland freshwater lake in Louisiana, Catahoula Lake covers approximately 119 km^2 and supports a variety of waterfowl. The lake is mainly fed by the Little River and drained by a 20-km, approximately 30-m wide man-made straight canal into the Black

River (Figure 4.1). There is a sluice gate at the outflow canal administered by the U.S. Army Corp of Engineers (USACE) to control the depth of Catahoula Lake, which is normally maintained low during the summer–fall period and high during the winter-spring period. The long-term average water depth is about 11 meters (Xu and Xu, 2018a). Backwater has been reported flowing from Mississippi-Atchafalaya-Red Rivers to the Catahoula Lake through the French Fork of Little River (Latuso et al., 2017; Xu and Xu, 2018a). There is a check dam

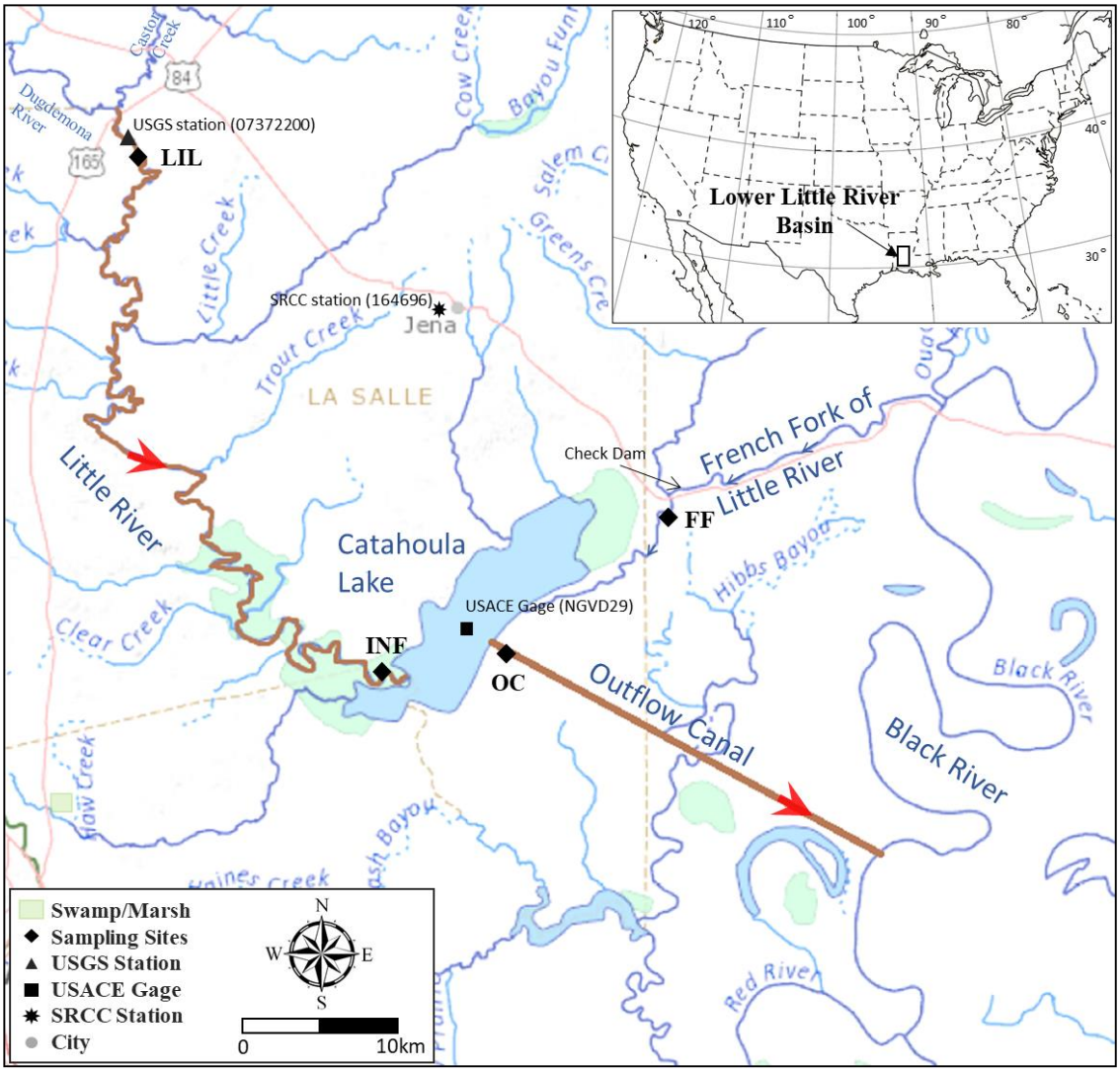

Figure 4.1. Geographical location of the Little River-Catahoula Lake continuum in subtropical Louisiana, United States. The flow directions of the major inflow and outflow for the Catahoula Lake are presented by arrowed red lines, while the direction of the backwater flow is shown by blue arrows.

located at the French Fork to control the backwater flow (Figure 4.1). A previous study has reported that Catahoula Lake had been receiving backwater in 2015 until August 12th, the day when the check dam was closed (Xu and Xu 2018a). Additionally, Catahoula Lake has been reported to historically receive more Mississippi River alluvial sediments and recently receive more Coastal Plain sediments from the Little River (Latuso et al., 2017). There is no known point source of metals in the studied river-lake continuum.

The studied region has a humid subtropical climate with a long-term annual precipitation and air temperature at around 1,470 mm and 20 °C, respectively (Xu and Xu, 2018b). During the study period, daily average air temperature fluctuated from -2 °C in February to 32 °C in August with an average of 19 °C, while precipitation amounted to 1496 mm, which is typical in this region (Figure 4.2). A series of clays, sands and gravels dominate the surface geology of the studied watershed lying unconformably on top of the Port Hudson and Citronelle formations (Fisk, 1939). Ruston and Smithdale series are the dominant soil series in the studied watershed (Web Soil Survey, 2015, Xu and Xu, 2018a).

4.2.2. Sampling Design

To track the dynamics of major and trace metals across the waterscape, we established four sites, LIL, INF, OC and FF, in the studied low-gradient river-lake continuum (Figure 4.1). Specifically, LIL was the Little River upstream site next to where Dugdemona River meets Castor Creek, while INF was lake inflow site situated at the western lakeshore wetland. Data from LIL to INF were used to determine the dynamics of metal transport in the Little River. OC was the lake outflow site located at the outflow canal, and data from INF to OC was utilized to understand the role of an in-network lake for the riverine metal transport. A backwater site, FF, was chosen at about 900 meters west of the check dam at French Fork of Little River to capture

possible effects from the backwater. The lake was assumed to be affected by the backwater effect from February 2015 to July 2015 during the study period (Figure 4.2, Xu and Xu, 2018a).

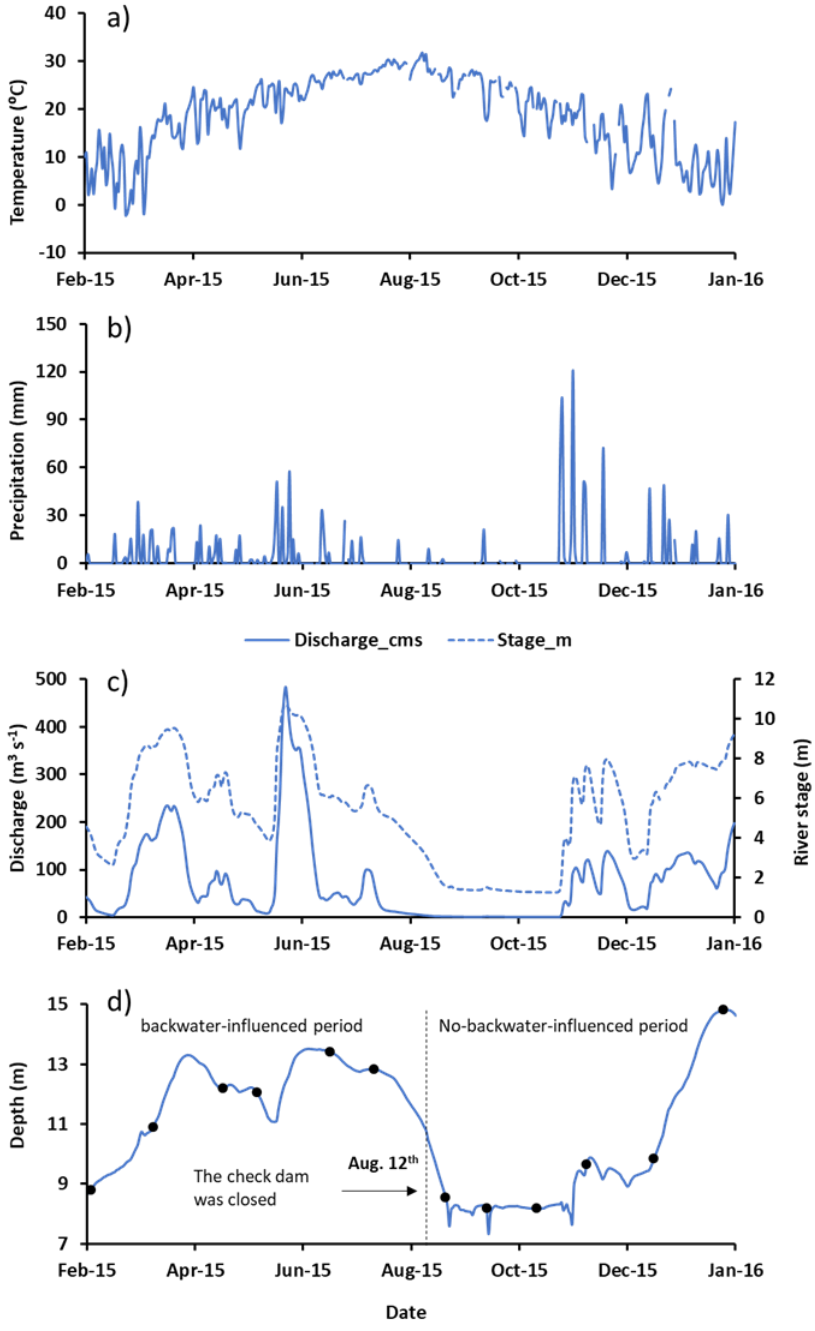

Figure 4.2. Daily air temperature a), precipitation b), Little River discharge and river stage c), and Catahoula Lake depth d) for the Little River-Catahoula Lake continuum from February 2015 to January 2016. For the figure at bottom, sampling dates are represented by black dots, while the day when the check dam at French Fork was closed (August 12th, 2015) is indicated by a dashed line.

4.2.3. In Situ Measurements and Water Sample Collection

All sites were sampled approximately monthly from February 2015 to January 2016 (Figure 4.2). During all field trips, in situ measurements and grab samples were taken at each site. A YSI 556 multi-probe meter (YSI Inc., Yellow Springs, OH, USA) was used to collect water quality parameters including water temperature, pH, and electrical conductivity (EC) at about 3 m from the shoreline. An AquaFluor® handheld fluorometer (Turner Designs, CA, USA) was also employed to measure in situ chlorophyll *a* fluorescence to explore the variability of algae activity. Water samples were taken approximately 40 cm below the water surface through a grab sampler consisting of a 3.7-m aluminum pole with a High-Density Polyethylene (HDPE) bottle attached at the end of the pole. All collected samples were stored in 250 mL thoroughly washed and acid bathed HDPE bottles. The samples were acidified to pH < 2 at the time of collection in the field for element analysis. Additional field quality control samples were taken at site OC (lake outflow). Immediately after collection, water samples were stored in a cooler with wet ice during the transportation and were frozen until analysis. Those samples were considered representative for the metal chemistry of water in the studied basin.

4.2.4. Water Sample Analysis

All water samples were analyzed for total recoverable concentrations (equivalent to total concentrations) of Ag, Al, As, Ba, Be, Bi, B, Ca, Cd, Cr, Co, Cu, Fe, K, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Si, Sn, Sr, Th, Ti, V, and Zn at the W.A. Callegari Environmental Center, Louisiana State University Agricultural Center following the protocol of the U.S. Environmental Protection Agency Method 200.7 (EPA, 1994). Specifically, each water sample was digested in a 50 mL tube with 47 mL sample solution, 1 mL metal-grade concentrated HCl and 2 mL metals-grade concentrated HNO_3 using a SC154 HotBlock® (Environmental Express, Charleston, SC,

USA) at 115 ºC. After 20 mL of the sample solution was evaporated, deionized water was added to the sample with 0.5 mL 1000-ppm yttrium as an internal standard. Once the total volume was brought back to 50 mL, 10 mL digested sample was filtered with 0.45 µm filters (Fox Scientific, Texas, USA). Element concentrations above the calibration curve were diluted by factors of 10, 20, 50, 100, or 1000 to bring them onto the calibration curve. The final analysis was conducted by an Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, Varian Vista MP-X, Palo Alto, CA, USA) for digested and filtered samples. Field and laboratory blanks, and independent/continuing calibration verification/blanks were used for quality control to ensure that the samples were not contaminated, and that all sample analyses were within control limits. The recovery rate of elements was measured by the laboratory control samples with known element concentrations. The recovery rate and method detection limits (MDL) of elements ranged from 87 to 128% and from 0.77 to 60 $mg \cdot L^{-1}$, respectively. Additional information on recovery rates and MDLs can be found in the supplemental information (Appendix D1).

4.2.5. Data Collection

During the study period, daily river discharge and gage height of the Little River was obtained from the U.S. Geological Survey (USGS) gauge station located close to the river upstream site (LIL) (station No.: 07372200, Figure 4.1). Daily water depths of Catahoula Lake were collected from the USACE gage# NGVD29 at the center of the lake (Figure 4.1). Climate data including daily air temperature and precipitation were gathered from the weather station at 92°7'29" W and 31°41'19" N, which was administered by the Southern Regional Climate Center (SRCC) (station ID.: 164696, Figure 4.1).

4.2.6. Data Analysis

The Weibull plotting position formula (Water Resources Council, 1981) was used to understand the relationship between the magnitude and frequency of daily discharge of the Little River. The depicted flow duration curve by the formula was used to determine the "high flows" and "low flows" conditions of the Little River. Specifically, if exceedance probabilities were greater than 90% and less than 10%, the corresponding flow conditions were classified as "low flows" and "high flows", respectively.

All statistical comparisons for element analysis were conducted with RStudio using the randomization test with a significance level of 0.05 (Edgington et al., 2007). Specifically, during the backwater-influenced period, two independent sample tests were conducted for statistical comparisons between sites FF (backwater from French Fork) and LIL (river upstream) and between sites FF and INF (lake inflow). All other tests between any two sites in the study were conducted as paired tests. For the backwater effect, if significant differences for average monthly metal concentrations or molar ratios were found between sites FF and INF, the effect was considered influential for the river-lake continuum. In addition, Pearson correlation coefficient (*r*) was used to detect correlations between metals in water.

4.3. RESULTS

4.3.1. Ambient Conditions

From February 1st, 2015 to January 31st, 2016, the Little River showed an average daily discharge of 71.3 $m^3 \cdot s^{-1}$ (median: 40.2 $m^3 \cdot s^{-1}$) ranging from 0.3 to 484.2 $m^3 \cdot s^{-1}$ (Figure 4.2). Specifically, daily discharge on the 12 sampling dates fluctuated from 0.3 to 161.1 $m^3 \cdot s^{-1}$ with an average of 5.3 m and a median of 5.5 m (Figure 4.2). There were two "high flow" events with the river discharge greater than 175 $m^3 \cdot s^{-1}$ occurring in March and May (March 13rd - 27th, 2015

and May 20th – June 7th, 2015), while "low flow" periods (river discharge less than 0.5 m^3 s^{-1}) only occurred in September and October. Average daily discharge on backwater-influenced period (95.4 $m^3 \cdot s^{-1}$) was significantly higher than that on the no-backwater-influenced period (47.6 $m^3 \cdot s^{-1}$, $p<0.001$). Specifically, average discharge on the sampling dates was 66.5 $m^3 \cdot s^{-1}$ in the backwater influenced period and 46.7 $m^3 \cdot s^{-1}$ in the no-backwater influenced period.

Catahoula Lake showed an average daily lake elevation of 11.0 m varying from 7.3 m to 14.8 m (Figure 4.2). Specifically, daily depth on the 12 sampling dates at the center of the lake ranged between 8.2 and 14.8 m. The lake was shallower in February and during late August - late October compared to the rest of the study period. Similar to the river discharge, average lake depth on backwater-influenced period (12.0 m) was significantly deeper than that on the no-backwater-influenced period (10.0 m, $p<0.001$). Average lake depth on the sampling dates was 11.7 m in the backwater influenced period and 9.9 m in the no-backwater influenced period, respectively.

For ambient parameters at all sites, water temperature varied seasonally corresponding to the changes in air temperature (Figure 4.2 and 4.3) with an average of around 20 °C during the study period. pH was in average slightly acidic, and chlorophyll *a* fluorescence was overall low in the late spring-early summer and high in the summer and fall (Figure 4.3). Specifically, the lake outflow (OC) site had an obvious drop in water temperature in September 2015, a dramatic increase in pH in March 2015 and very high chlorophyll *a* fluorescence levels in September-October 2015. Also, electrical conductivity at the Little River upstream (LIL) was very high in September and October 2015.

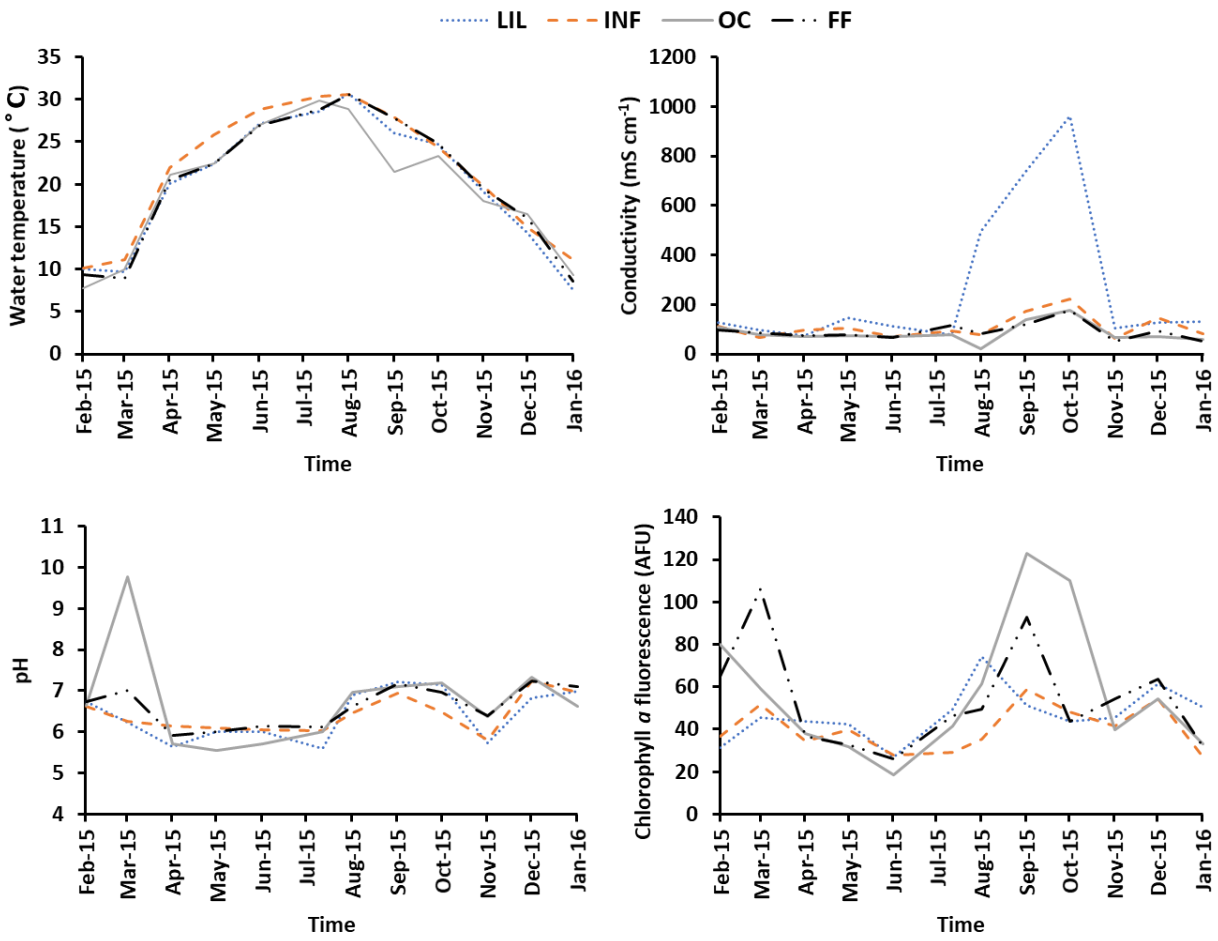

Figure 4.3. Seasonal variations of water temperature, electrical conductivity, pH and chlorophyll a fluorescence at all sites during February 2015 - January 2016.

4.3.2. Dynamics of Metal Concentrations and Molar Ratios in The River-lake Continuum

Based on average monthly concentrations, among all 29 metals analyzed in this study, 6 metals including Al, Ca, Fe, K, Mg and Na constituted more than 98% portion of the pool, while 5 metals including B, Ba, Mn, Sr and Ti were amounted to the rest 1-2% (Table 4.1). Other metals were excluded for analysis due to their low concentrations. From the Little River upstream to the lake inflow, all average monthly metal concentrations showed significant decreases (n=12). A significant increase was found in average monthly Si/Al ratio from the Little River upstream and lake inflow (Table 4.1 and Figure 4.4). Also, at the river upstream P

concentrations were strongly correlated with Fe (r=0.91, p<0.001) and Ca (r=0.72, p=0.012) concentrations. However, these correlations no longer existed at the lake inflow (r=0.30, p=0.34 for Fe and P, r=0.47, p=0.12 for Ca and P).

Table 4.1. Average monthly element concentrations and molar ratios (mean ± standard deviation) at sites LIL (Little River upstream), INF (lake inflow) and OC (lake outflow) during February 2015 - January 2016. P-values were only shown for significant changes (p < 0.05) in element concentrations or molar ratios among sites (significant increases were in *italics*).

	Sites			P-value		
	LIL	INF	OC	LIL to INF	INF to OC	LIL to OC
Major element concentrations (mg L^{-1}, n = 12)						
Al	2.6 ± *1.3*	1.9 ± *1.2*	3.3 ± *2.9*	0.03	*0.03*	
Ca	8.5 ± *4.2*	5.4 ± *1.2*	5.7 ± *1.9*	0.003		0.002
Fe	3.0 ± *1.1*	2.1 ± *0.5*	2.9 ± *2.0*	0.03		
Mg*	2.1 ± *1.0*	1.5 ± *0.3*	1.9 ± *0.6*	0.003	*<0.001*	
K	3.8 ± *2.5*	2.4 ± *0.4*	2.8 ± *0.6*	0.01	*0.04*	
Si	5.7 ± *2.3*	5.3 ± *2.6*	7.1 ± *4.9*			
Na*	36.0 ± *50.0*	11.5 ± *7.5*	7.5 ± *4.9*	0.03	0.003	<0.001
Other element concentrations (µg L^{-1}, n = 12)						
B	70 ± *66*	32 ± *9*	31 ± *8*	<0.001		<0.001
Ba	79 ± *32*	57 ± *6*	67 ± *27*	<0.001		
Mn	385 ± *411*	169 ± *116*	191 ± *138*	<0.001		0.01
P*	127 ± *72*	89 ± *25*	121 ± *47*		*0.002*	
Sr	121 ± *86*	66 ± *17*	61 ± *20*	0.004		<0.001
Ti	39 ± *44*	26 ± *22*	46 ± *30*	0.04	*<0.001*	
Molar ratios (n = 12)						
Si/Al	2.7 ± *1.7*	3.5 ± *2.0*	3.6 ± *3.7*	*0.05*		
Ca/Mg*	2.5 ± *0.6*	2.3 ± *0.5*	1.9 ± *0.4*		<0.001	<0.001
Ba/Sr	0.5 ± *0.1*	0.6 ± *0.1*	0.7 ± *0.1*		*<0.001*	*0.04*

* Influenced by the backwater during February 2015 - July 2015.

Significant increases in average monthly concentrations of Al, Mg, K and Ti were observed from the lake inflow to outflow (Table 4.1 and Figure 4.5). Specifically, these increases were very obvious in September and October 2015 for all metals (Figure 4.5). Also, from the lake inflow to the outflow, a constant decrease was observed for Ba/Sr molar ratio (Figure 4.4

and Table 4.1), while a significant decrease was found for average monthly Ca/Mg molar ratios (Table 4.1). Only Ca, Na, B, Mn and Sr were found to have significant decreases across the river-lake continuum (Table 4.1).

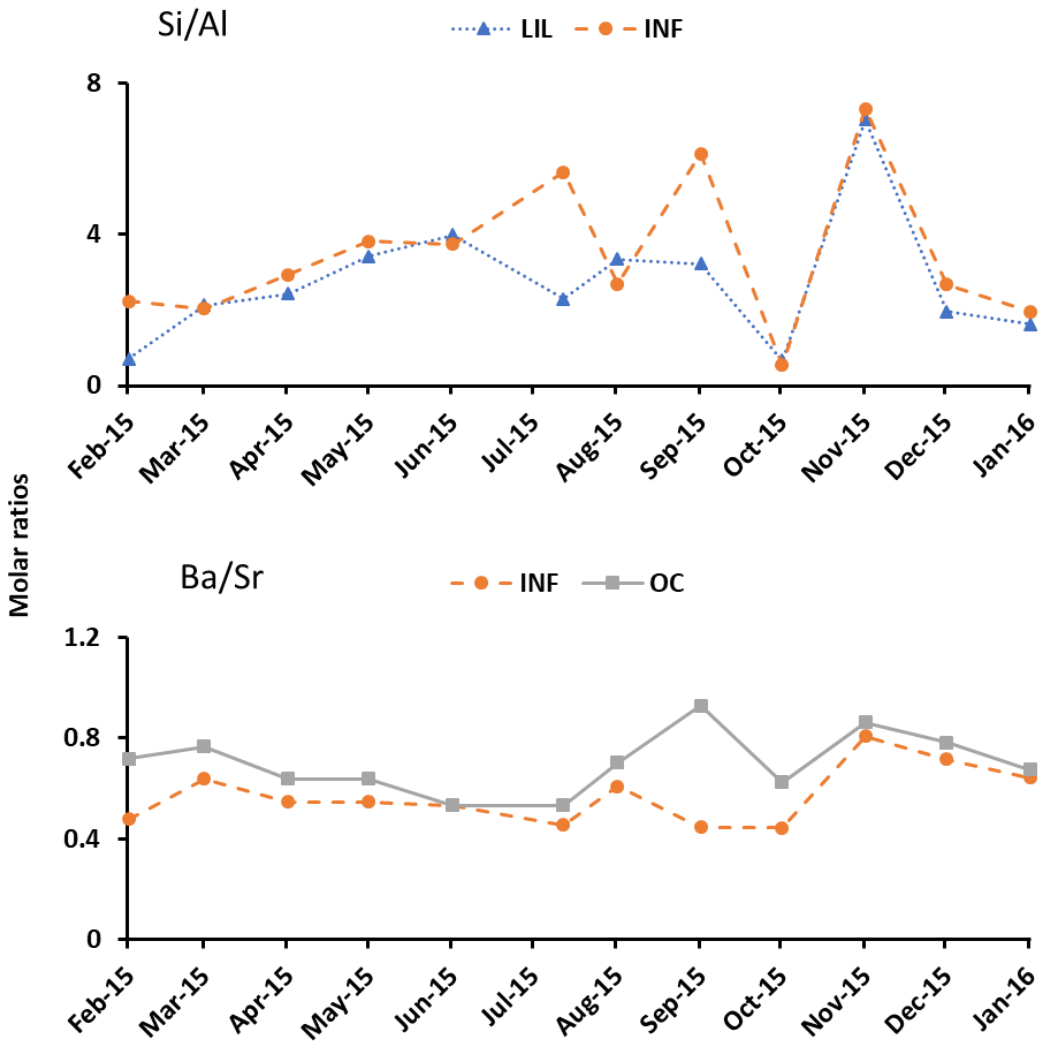

Figure 4.4. Seasonal variations of silicate to aluminum molar ratios at sites LIL (Little River upstream) and INF (lake inflow), and barium to strontium molar ratios at sites INF (lake inflow) and OC (outflow).

4.3.3. Backwater Effects

The backwater seemed to directly affect Mg and Na transports in the river-lake continuum during the backwater-influenced period. Specifically, the backwater effect was profound on Mg as average monthly Mg concentrations in both lake inflow and outflow were

significantly lower than their counterpart in the backwater (Table 4.2 and Figure 4.5). In contrast, the lake inflow had a significant higher average monthly Na concentration than that in the backwater (Table 4.2). No significant difference in average monthly Na concentrations was found between lake outflow and the backwater. In addition, the backwater had a significantly lower average monthly Ca/Mg ratio than those in the lake inflow and outflow (Table 4.2).

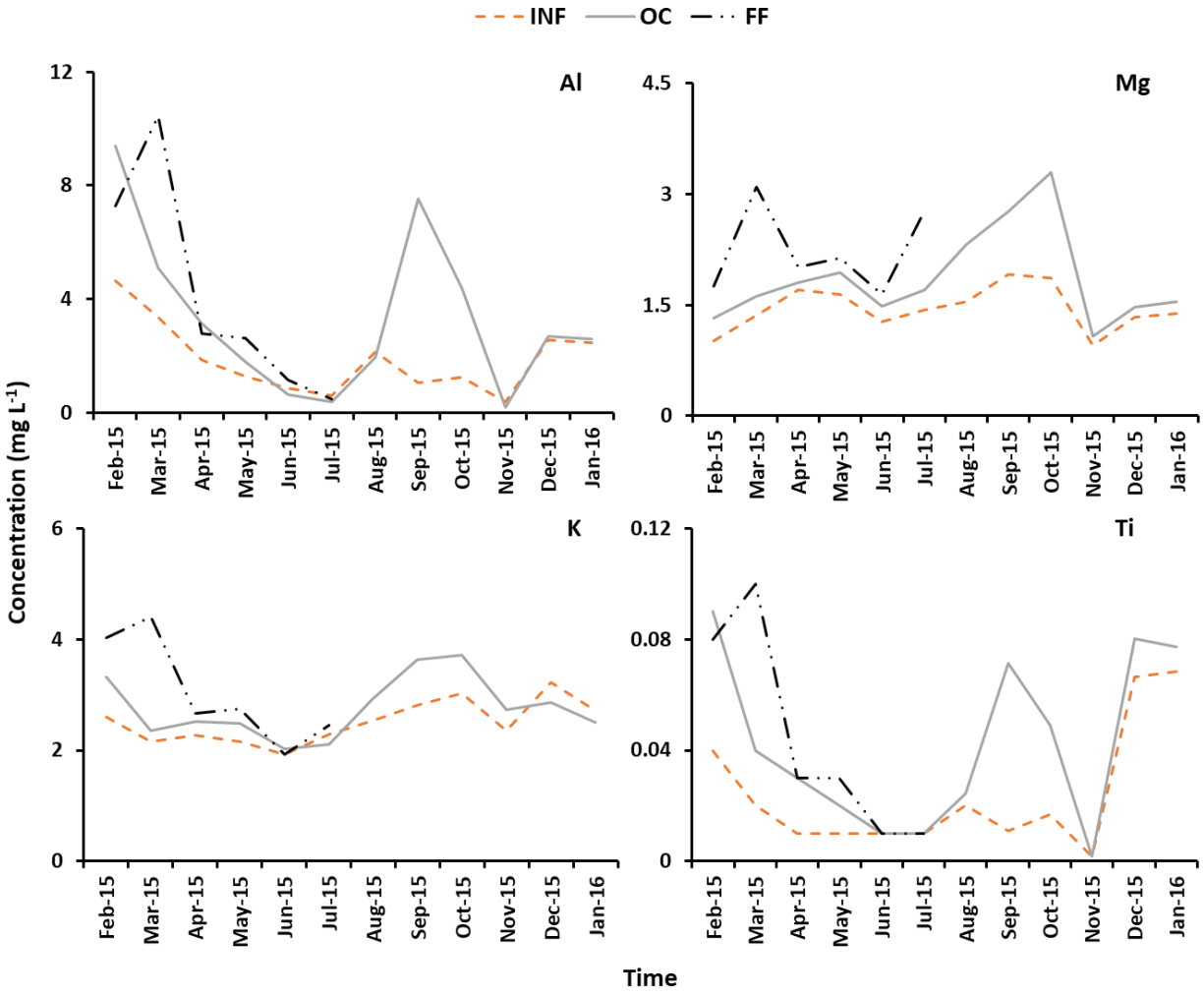

Figure 4.5. Seasonal variations of aluminum, magnesium, potassium and titanium at sites INF (lake inflow), OC (outflow) and FF (backwater) during February 2015 - January 2016. The site FF (backwater) was only shown for the backwater-influenced period (from February 2015 to July 2015).

Table 4.2. Average monthly concentrations and molar ratios (mean ± standard deviation) of metals influenced by the backwater effect at sites INF (lake inflow), OC (lake outflow) and FF (backwater) during the backwater-influenced period (from February 2015 to July 2015) and the no-backwater-influenced period (from July 2016 to January 2016). P-values were only shown for significant changes ($p < 0.05$) in metal concentrations or molar ratios among sites.

	Sites			P-value		
	INF	OC	FF	INF to OC	FF to OC	FF to INF
Backwater influenced period (n = 6)						
Mg	1.4 ± *0.3*	1.6 ± *0.2*	2.2 ± *0.6*	<0.001	0.03	0.002
Na	8.6 ± *3.3*	6.1 ± *3.5*	5.2 ± *1.5*			0.03
Ca/Mg	2.3 ± *0.7*	1.9 ± *0.5*	1.7 ± *0.5*	<0.001	<0.001	<0.001
No-backwater influenced period (n = 6)						
Mg	1.5 ± *0.4*	2.1 ± *0.9*		<0.001		
Na	14.4 ± *9.6*	8.8 ± *5.9*		<0.001		
Ca/Mg	2.3 ± *0.2*	1.9 ± *0.1*		<0.001		

4.4. DISCUSSIONS

4.4.1. The River as A Sink for Metals

Findings from this study suggest that the Little River functions as a sink for all observed metals, and one of the most possible mechanisms is sedimentation. Specifically, the large decrease in the correlations between metals (Fe and Ca) and P from the river upstream to the lake inflow could be attributed to sedimentation of calcium carbonate and iron oxyhydroxide. High correlations between metals (Fe and Ca) and P at the Little River upstream indicated that phosphorus from headwaters were mostly associated with calcium carbonates and bound onto metal oxides, while their corresponding low correlations at the lake inflow showed that remaining phosphorus there may mainly exist as free phosphate or refractory organic phosphorus due to the sink of metal oxides in the riverine transport. Also, metals such as Al, Ba, Fe, Mn and Ti could settle out by either precipitating as inorganic compounds or bounding to other particulate matters (Sheoran and Sheoran, 2006). The flat geomorphology of the region and sluggish flow of the Little River could contribute to this process, especially during the months

with the continuous “low flow” condition (Rossin et al., 1983; Kozerski, 2003). Sedimentation has long been recognized as the principle process in removal of metals in other aquatic systems (Hupp et al., 1993; Sheoran and Sheoran, 2006), and similar sink function of the river has been reported in the same region. For instance, Reiman and others (2018) found that the Atchafalaya River in Louisiana, United States, acted as a sink for nearly all metals observed in their study. They mainly attributed that to sedimentation as the Atchafalaya River had been shown to trap large amount of sediments annually (Rosen and Xu, 2015; Reiman et al., 2018).

Like sedimentation, biological removal can also make the river a metal sink through root adsorption and uptake. The annual variation of the river stage promotes the growth of herbaceous wetland plants in the studied watershed (Latuso, 2014), which have been reported to have a much higher metal uptake rate (Sheoran and Sheoran, 2006). Denny (1980) and Greenway (1997) noted that wetland plants played a very important role in metal removal, the main route of which was through roots in emergent and surface-floating. In addition, high biological demand for Ca, Mg, K and Na during the growing season usually results in strong assimilation of these nutrients into the biomass and productivity of aquatic organisms (Likens, 2010). The algal gloom in the Little River during the summer with an increase of chlorophyll *a* could contribute to this process.

Weathering of minerals was evident in the Little River, but its source effect seemed to be overwhelmed by other sink effects. The significant increase in Si/Al ratio from river upstream to the lake inflow could suggest constant silicate weathering in the Little River since Si and Al are the two main elements associated with the aluminosilicates (Figure 4.4). Specifically, silicate minerals presented as aluminosilicates could have different degrees of weathering from feldspars minerals to meteorized clays, the chemical weathering of which usually comes through incongruent dissolution. Globally this process releases Si and K to the water but Al remains in

the solid phase (Tardy et al., 2004). This agrees with previous studies reporting that sediment loads carried by the Little River are strongly acidic and Coastal Plain sediments (Kilpatrick et al., 1986) containing lots of kaolinite clays formed by chemical weathering in situ (Sionneau et al., 2008). Also, the release of Ca and Mg through carbonate weathering has been reported in a previous study taken at the same watershed, which is especially obvious during low flow periods (Xu and Xu, 2018a).

4.4.2. Catahoula Lake Acting as A Source for Metals

Catahoula Lake acted as a source for certain metals (Al, Mg, K and Ti), which could be primarily attributed to the specific components of lake sediments. Previous studies have reported the enrichment of certain metals in the lakebed. For example, Milne and Earley (1958) found that Catahoula Lake historically received a greater input of Mississippi River alluvial sediments, which are high in smectitic clays, have high cation exchange capacity, and retain high concentrations of basic cations such as K^+ (Milne and Earley, 1958). Latuso and others (2017) observed the high concentration of Ti at the surface of the lakebed sediments. They attributed that to the recent dominance of Little River input with Coastal-Plain sediments enriched in Ti (Latuso et al., 2017). Also, frequent redistribution of sediments after initial deposition has been reported in the lake as the sedimentation was fairly uniform across the lakebed, probably due to waves and bioturbation from waterfowl (Peters and Afton, 1993; Latuso et al., 2017). It is worth noting that the fall turnover could play a major role affecting seasonal dynamics of these metals which were re-distributed in the hypolimnion zone and sediments throughout the water column as the water mixed. This can be evidenced by the obvious cooling of water temperature at the lake outflow in September (Figure 4.3) and the great differences in metal concentrations between the lake inflow and outflow during September-October (Figure 4.5). Similar conditions have

been observed in few other studies. For instance, in a study of the geochemistry of a warm monomictic lake (Lake Texoma) in northern Texas, United States, Sun and others (2016) reported that the summer stratification and fall turnover were responsible for vertical variations in concentration of Fe, Mn and other trace elements in the lake water column (Sun et al., 2016).

At the same time, Catahoula Lake seemed to have a greater weathering intensity than the river, which leads to a greater release of metals to the water column. Specifically, although Ba and Sr account for a small portion of the alkaline earth metals, variations in their molar ratios indicate changes in the weathering intensity. Ba and Sr occur in different minerals with different weathering susceptibility. For instance, Ba is often rich in the geographic areas characterized by volcanic terrains, specifically alkaline-rich volcanic products or sedimentary volcanic by-products (e.g. Cuoco et al., 2013). In weathering, Sr substitutes for Ca or K, whereas Ba usually substitutes for K (Mason and Moore, 1982). Since the K-minerals in granitoids are more resistant to weathering than the Ca-minerals, the release of Ba to soil solution demands a more intensive weathering than the release of Sr (Land et al., 2000). In this case, the increase of Br/Sr ratio at the lake outlet suggests an increased weathering intensity in the Catahoula Lake.

Backwater could also have an impact leading to the metal increases at the lake outflow. On one hand, during the backwater-influenced period, a significant enrichment of Mg was observed in the backwater flowing from Mississippi-Atchafalaya-Red Rivers to the Catahoula Lake through the check dam (Figure 4.5 and Table 4.2). On the other hand, based on the mass loads of total recovery Ca and Mg, Ca/Mg molar ratio in the Mississippi-Atchafalaya River water during 2013-2016 was around 1.80 (Reiman et al., 2018), which is close to the Ca/Mg ratio observed at the backwater site and about 22% lower than the ratio at the lake inflow during the

backwater-influenced period (Table 4.2). Since the inlet of backwater is close to the lake outflow, its effects on the lake output could be profound.

4.5. CONCLUSIONS

This study investigated the spatial and seasonal dynamics of total recoverable concentrations and molar ratios of major and trace metals in a river-lake continuum in the low-gradient, subtropical Louisiana, United States, to understand the metal chemistry of water across the waterscape. The findings from the study show that six major metals (Al, Ca, Fe, K, Mg and Na) constituted more than 98% portion of the pool, while five others (B, Ba, Mn, Sr and Ti) were amounted to the rest 1-2%. The river functioned as a sink for metals evidenced by significant decreases in average monthly concentrations of all metals from the river upstream to the lake inflow. This could be attributed to sedimentation indicated by changes in correlations between P and Fe/Ca in the riverine transport and biological uptake especially in the summer algal bloom in the river. Although overwhelmed by these sink effects, chemical weathering in situ of minerals were also found with a significant increase in Si/Al molar ratio along the river corridor. In contrast, Catahoula Lake acted as a source for Al, Mg, K and Ti, the average monthly concentrations of which were significantly increased from the lake inflow to the outflow. This could be mainly attributed to the specific components of the lake sediments that were frequent re-distributed after deposition. Also, indicated by the significant increase in average Ba/Sr molar ratio from lake inflow to the outflow, the lake could have a greater weathering intensity than the river with more metals released to the water column. The backwater could also contribute to the source function of the lake, which constantly contained significantly high Mg concentration from the Mississippi-Atchafalaya-Red Rivers. Since the role of the lake within the connected fluvial network in this study is highly related with the lake's own features, future studies for other in-

network lakes with different depths and at different climate regions would be beneficial for a further understanding of metal chemistry of water in a river-lake continuum.

CHAPTER 5. SUMMARY AND CONCLUSIONS

This dissertation research investigated element transports in a river-lake continuum across a forest-dominated landscape, taking the Little River Basin in subtropical Louisiana, USA as a case study. Three interconnected studies were taken to 1) determine whether the current forestry BMPs of Louisiana are effective in reducing sediment, nitrogen, and phosphorus levels and loads from forest-dominated river headwaters, 2) investigate the major sources and corresponding biogeochemical processes controlling DIC and DOC dynamics in a river-lake continuum and explore whether the in-network lake function as a carbon sink or carbon source for dissolved carbon transport across the waterscape, and 3) assess the spatial and seasonal dynamics of major and trace metal concentrations and their atomic ratios from a river upstream to the outlet of its downstream receiving lake and elucidate whether the lake and river act as a source or a sink for metal dynamics. Major findings from this research are summarized below.

The study conducted on the headwaters of the Little River Basin compared long-term concentrations and loadings of TSS, nitrate/nitrite nitrogen (NO_3NO_2-N), TKN, and TP before (1978-1988) and after extensive implementation of forestry BMPs (1994-2008). Results show that after extensive BMP implementation, both concentrations and loads of TSS in the basin outlet decreased significantly from 34 to 25 mg L^{-1} and from 55,000 to 36,700 t $year^{-1}$, respectively. However, no significant difference was found in NO_3NO_2-N, TKN, and TP concentrations between the two periods. The results of nutrient loadings varied, whereby the annual nitrogen loading declined without significant differences (from 1,790 to 1,600 t $year^{-1}$ for TKN and from 176 to 158 t $year^{-1}$ for NO_3NO_2-N, respectively) but the annual TP loading increased significantly (from 152 to 192 t $year^{-1}$) after BMP implementation. Increases in TP loading are likely due to an increased application of phosphorus fertilizer, which offset BMPs'

effects especially during high flow conditions. These results strongly suggest that current forestry BMPs in this region are effective in reducing sediment loading, but current BMP guidelines for fertilization and nutrient management need to be reviewed and improved.

The study assessing carbon biogeochemistry along the Little River-Catahoula Lake continuum conducted monthly in-situ measurements and water sample collections at four locations in the Lower Little River Basin during April 2015 to February 2016 to determine riverine carbon transport into and out of the lake. Results show that much of the DIC in the river-lake continuum originated from ^{13}C depleted sources with an average $\delta^{13}C_{DIC}$ of -18.5‰. Significant decreases in DIC were found after the river passed through the lake (from 482 to 399 μmol L^{-1}), which was most prevalent when the lake was not affected by backwater flow from the downstream river. CO_2 outgassing could be mainly responsible for the sink behavior of the lake for DIC. DOC in the studied watershed were mostly terrigenous with low $\delta^{13}C_{DOC}$ averaged at -29.2‰. Significant, consistent decreases in DOC concentrations were found from the river to the lake inflow and then to the lake outflow. During the majority of the year, the lake reduced DOC concentrations from the river inflow water, but switched to functioning as a source of DOC during warmer, dryer conditions in September and October due to increased water residence time. Therefore, the lake functioned both as a sink and as a source for DOC.

The study investigating metal dynamics along the low-gradient Little River-Catahoula Lake continuum analyzed total recoverable metal concentrations from water samples collected monthly at four locations same as the previous one during February 2015 - January 2016 to understand metal biogeochemistry across the waterscape. Results show that six major metals (Al, Ca, Fe, K, Mg and Na) constituted more than 98% portion of the pool based on average monthly metal concentrations, while five others (B, Ba, Mn, Sr and Ti) were amounted to the rest 1-2%.

Significant decreases in average monthly concentrations of all metals were detected from river upstream to lake inflow, indicating that the Little River functioned as a sink for metal transport which could be attributed to sedimentation and biological immobilization. In contrast, significant increases in average monthly concentrations of Al, Mg, K and Ti were found between lake inflow and outflow. Enrichments of these metals in the lakebed sediments and the greater weathering intensity at the lake were considered as the main causes driving metal increases. In addition, the backwater to the lake also contributed to the lake source effect as it contained a significantly higher Mg.

This dissertation research fills in the knowledge gap of effects of human disturbances and the role of an in-network lake for element transports in a forested river-lake continuum. It is only an ongoing step to expand and address deficiencies of the classic river continuum concept. There is a closely connected transitional zone between the terrestrial ecosystem and the open ocean consisting of pore waters, streams, creeks, groundwater, springs, aquifers, lakes, rivers, wetlands and estuaries, through which a sequence of geological, physical, chemical and biological systems transport, transform and deliver elements during their transit from headwaters to oceans. Many factors including temperature, precipitation and landscape features can affect the dynamics of elemental transports along the aquatic continuum, and future studies on other types of landscapes and at other climate regions will be beneficial for an improved understanding, interpreting and modeling of network-scale or regional-scale element dynamics in these systems. In addition, more applications of novel statistical methods such as neural networks and Bayesian statistics should be encouraged, which can go beyond traditional based laboratory, monitoring, or analytical techniques to better disentangle the multiple influences that occur throughout aquatic continua. With more integration and a further understanding of the mechanistic foundations of

patterns across the aquatic continuum, we will be better prepared to use and apply aquatic continuum concepts for future restoration and management projects.

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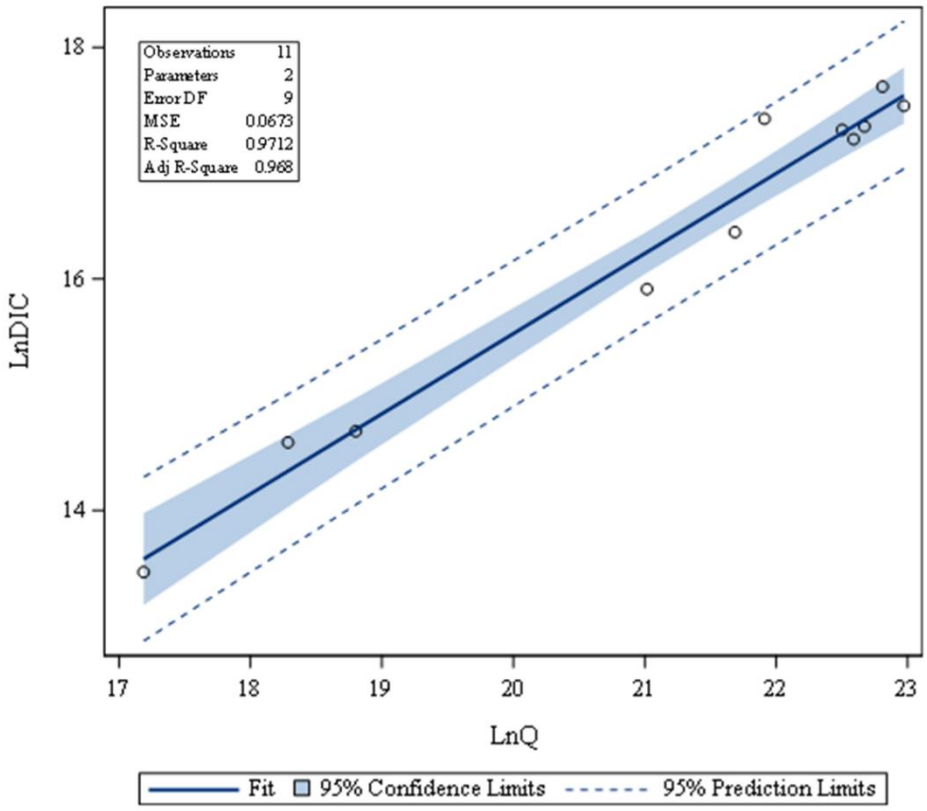
APPENDIX B. PERMISSION TO REPRINT CHAPTER 3

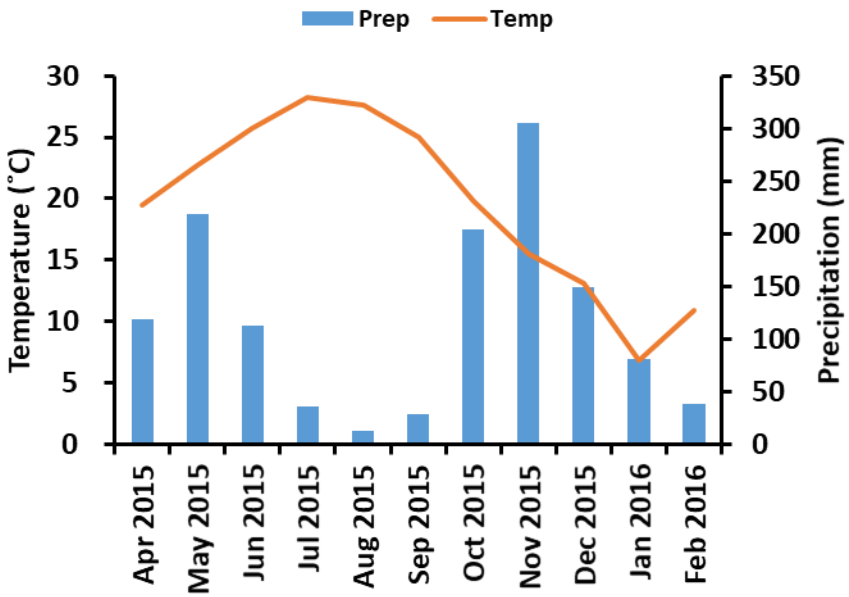
APPENDIX C. SUPPLEMENTARY INFORMATION FOR CHAPTER 3

Appendix C1. Statistics of parameterization (b_0 and b_1) for Equation (2), root mean square error (RMSE), results of the Shapiro-Wilk test, and the log bias correction factor (BCF). The equation was used to estimate daily loads of dissolved inorganic carbon (DIC) at the Little River site (LIL).

	b_0	b_1	RMSE	Shapiro-Wilk normality test		BCF
				W	P-value	
DIC	1.68	0.69	0.26	0.93	0.38	1.08



Appendix C2. Statistical performance of the rating curve (Appendix C1) for estimating DIC daily mass loads of the Little River. The X axis are ln(Qday) and the Y axis are ln(DICr) in Equation (3.2).



Appendix C3. Average monthly precipitation and temperature in the studied watershed during April 2015 to February 2016.

APPENDIX D. SUPPLEMENTARY INFORMATION FOR CHAPTER 4

Appendix D1. Method detection limits (MDL) in µg L-1 for elements analysis and their recovery rates (%) found in laboratory control samples (LCS) recovery analysis.

Element	MDL (µg L^{-1})	n	Recovery Rates (%)
Aluminum	60	12	87-113
Antimony	10	12	98-112
Arsenic	10	12	95-109
Barium	20	12	67-111
Beryllium	10	12	97-109
Bismuth	10	12	97-137
Boron	20	12	95-114
Cadmium	10	12	96-109
Calcium	20	12	83-112
Chromium	10	12	96-108
Cobalt	10	12	97-109
Copper	10	12	97-109
Iron	10	12	97-130
Lead	10	12	96-109
Lithium	3.7	12	95-111
Magnesium	10	12	56-108
Manganese	10	12	97-108
Molybdenum	38	12	98-110
Nickel	10	12	96-109
Phosphorus	24	12	95-128
Potassium	32	12	97-116
Selenium	10	12	95-110
Silicon	7	12	83-152
Silver	7	12	97-108
Sodium	29	12	78-111
Strontium	0.77	12	97-108
Thallium	10	12	48-109
Tin	10	12	100-115
Titanium	3.8	12	98-110
Vanadium	10	12	98-108
Zinc	10	12	97-109

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